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Mathematics. — *"Ueber projektive Differentialinvarianten"*. IV. Von Prof. R. WEITZENBÖCK.

(Communicated at the meeting of February 28, 1925).

In dieser Mitteilung wird das Problem der Bestimmung aller projektiven Differentialinvarianten J einer m-dimensionalen Mannigfaltigkeit, die in einem linearen Raume von $m+1$ Dimensionen liegt, auf eine Frage der Tensorrechnung zurückgeführt: Bestimmung der Invarianten einer Reihe "projektiver" Tensoren. Man erhält diese Reduktion auf eine ganz naturgemässe Weise, wenn man von den Eigenschaften G, P und H von J Gebrauch macht (Vgl. die erste Mitteilung).

Unsere Methode vereinigt die durch E. J. WILCZYNSKI [1]) bei $m=2$ und allgemein durch G. FUBINI [2]) eingenommenen Standpunkte und kann unmittelbar bei den affinen Differentialinvarianten angewendet werden, wenn wir z.B. $y_{m+2} \equiv 1$ setzen.

§ 1.

Eine projektive Differentialinvariante J hat, vgl. den Anfang der ersten Mitteilung, erstens die Eigenschaft G (Invarianz bei den linearen homogenen Transformationen

$$\zeta_i = a_{1i} x_1 + a_{2i} x_2 + \ldots + a_{ni} x_n \,)$$

und ist daher eine Funktion von Klammerfaktoren $(y_{\alpha_1} y_{\alpha_2} \ldots y_{\alpha_{m+2}})$.

Wir setzen wieder voraus dass

$$A = |(v' y_{ik})| = |(y y_1 \ldots y_m y_{ik})| \neq 0 \quad \ldots \ldots \quad (1)$$

ist. Dann sind nicht alle Klammerfaktoren $(y y_1 \ldots y_m y_{ik})$ Null und wir können z.B. $(y y_1 \ldots y_m y_{\alpha\beta}) \neq 0$ voraussetzen, wo α und β fest gewählt sind.

Mit Hilfe der Identität ($\nu =$ Ziffernkomplex)

$$\left.\begin{aligned} (y y_1 \ldots y_m y_{\alpha\beta})\, y_\nu = {} & (y_\nu y_1 \ldots m_m y_{\alpha\beta})\, y + \\ & + (y y_\nu y_2 \ldots y_m y_{\alpha\beta})\, y_1 + \ldots + (y y_1 \ldots y_m y_\nu)\, y_{\alpha\beta} \end{aligned}\right\} \quad . \quad (2)$$

ist dann jeder Klammerfaktor $(y_{\nu_1} y_{\nu_2} \ldots y_{\nu_{m+2}})$ ausdrückbar durch $(y y_1 \ldots y_m y_{\alpha\beta})$ und die Klammerfaktoren

$$(y_\nu y_1 \ldots y_m y_{\alpha\beta}),\ (y y_1 \ldots y_{i-1} y_\nu y_{i+1} \ldots y_m y_{\alpha\beta}),\ (y y_1 \ldots y_m y_\nu). \quad . \quad (3)$$

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[1]) E. J. WILCZYNSKI, Trans. Amer. Math. Soc. 8 (1907), p. 233; ibid. 9 (1908), p. 79; ibid. 10 (1909), p. 176.

[2]) G. FUBINI, Rend. di Palermo 43 (1918), p. 1. Ausführliche Litteratur in dem dieser Tage erscheinenden Artikel III D. 11 der „Enzyclopädie" von L. BERWALD (Nr. 10 bis 12).

Wiederholte Anwendung dieses Resultates und der Gleichung

$$\left.\begin{aligned}(y_{i_1}\ldots y_{i_{m+1}}y_\nu)=\frac{\partial(y_{i_1}\ldots y_{i_{m+1}}y_{\nu-1})}{\partial t_j}-(y_{i_1+1}\,y_{i_2}\ldots y_\nu)-\\ -(y_{i_1}\,y_{i_2+1}\,y_{i_3}\ldots y_\nu)-\ldots-(y_{i_1}\ldots y_{1+i_{m+1}}\,y_\nu)\end{aligned}\right\}\quad.\quad.\quad(4)$$

gibt dann: jeder Klammerfaktor und deshalb auch jede Invariante ist ausdrückbar durch die Funktionen

$$\left.\begin{aligned}\varphi_1&=(yy_1\ldots y_m\,y_{ik}) & \varphi_4&=(yy_1\ldots y_m\,y_{ikl})\\ \varphi_2&=(y_{ik}y_1\ldots y_m\,y_{rs}) & \varphi_5&=(y_{rs}\,y_1\ldots y_m\,y_{ikl})\\ \varphi_3&=(y_{ik}\,y_1\ldots y\ldots y_m\,y_{rs}) & \varphi_6&=(y_{rs}\,y_1\ldots y\ldots y_m\,y_{ikl})\end{aligned}\right\}\quad.\quad.\quad(5)$$

und deren Ableitungen.

Hiebei ist in φ_3 und in φ_6 die Reihe y_h durch y ersetzt $(h=1,2,\ldots,m)$.

J ist zweitens invariant bei Parametertransformationen

$$t_i=t_i(\bar{t}_1,\ldots,\bar{t}_m)\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad(6)$$

und kann daher als Eliminationsresultat betrachtet werden, erhalten bei der Elimination der Ableitungen

$$\frac{\partial t_i}{\partial\bar{t}_\lambda},\quad\frac{\partial^2 t_i}{\partial\bar{t}_\lambda\,\partial\bar{t}_\mu},\ldots.$$

aus den Transformationsgleichungen der Funktionen (5) und ihrer Ableitungen. So haben wir z.B. bei φ_1:

$$\bar{y}_i=y_\lambda\,.\,\frac{\partial t_\lambda}{\partial\bar{t}_i}\quad,\quad\bar{y}_{ik}=y_{\lambda\mu}\frac{\partial t_\lambda}{\partial\bar{t}_i}\,\frac{\partial t_\mu}{\partial\bar{t}_k}+y_\lambda\frac{\partial^2 t_\lambda}{\partial\bar{t}_i\,\partial\bar{t}_k}\quad:$$

$$\overline{(\varphi_1)}_{ik}=(\varphi_1)_{\lambda\mu}\,.\,\frac{\partial t_\lambda}{\partial\bar{t}_i}\,.\,\frac{\partial t_\mu}{\partial\bar{t}_k}\,.\,\triangle.$$

Die Aufgabe: Elimination der $\dfrac{\partial^s t}{\partial\bar{t}^s}$ aus den Transformationsgleichungen der Funktionen φ_i und ihrer Ableitungen wird nach FUBINI sehr vereinfacht, wenn wir die φ_i ersetzen durch Funktion ψ_i, die an Stelle der partiellen Ableitungen y_{ik}, $y_{ikl},\ldots$ kovariante Ableitungen $y_{i(k)}$, $y_{i(k)(l)},\ldots$ enthalten. Dies setzt die Kenntnis einer quadratischen Fundamentalform $g_{ik}\,dt^i dt^k$ mit nicht-verschwindender Diskriminante $g=|g_{ik}|\neq 0$ und vom $\triangle$-Gewichte Null voraus. Eine solche Form ist aber hier vorhanden:

$$f_2=g_{ik}\,dt^i\,dt^k=\frac{F_2}{\sqrt[m+2]{A}}\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad(7)$$

Wir haben

$$\bar{f}_2=f_2\quad,\quad\tilde{f}_2=\lambda^2 f_2\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad.\quad(8)$$

d.h. f_2 hat das $\triangle$-Gewicht Null und das λ-Gewicht 2. g_{ik} gibt also im

Parameterraum $(t_1, t_2, \ldots, t_m)$ einen kovarianten Tensor zweiter Stufe.

Mit Rücksicht auf die zweite der Gleichungen (8) sagen wir, dass g_{ik} ein "projektiver" Tensor mit λ-Gewicht 2 ist. Dagegen ist F_2 eine "projektive Tensordichte" mit $\triangle$-Gewicht 1 und λ-Gewicht $m+2$.

Tensoren des t-Raumes, die bei $\tilde{y} = \lambda y$ invariant sind, nennen wir "projektive" Tensoren.

§ 2.

An Stelle von (5) nehmen wir nun die folgenden Funktionen:

$$\left.\begin{aligned}
\psi_1 &= (y y_1 \ldots y_m y_{i(k)}) \cdot A^{-\frac{1}{m+2}} = g_{ik} \\
\psi_2 &= (y_{i(k)} y_1 \ldots y_m y_{r(s)}) \cdot A^{-\frac{1}{m+2}} = \varphi_{ik,rs} \\
\psi_3 &= (y_{i(k)} y_1 \ldots y \ldots y_m y_{r(s)}) \cdot A^{-\frac{1}{m+2}} = \alpha^h_{ik,rs} \\
\psi_4 &= (y y_1 \ldots y_m y_{i(k)(l)}) \cdot A^{-\frac{1}{m+2}} = h_{ik,l} \\
\psi_5 &= (y_{r(s)} y_1 \ldots y_m y_{i(k)(l)}) \cdot A^{-\frac{1}{m+2}} = \vartheta_{rs,ik,l} \\
\psi_6 &= (y_{r(s)} y_1 \ldots y \ldots y_m y_{i(k)(l)}) \cdot A^{-\frac{1}{m+2}} = \eta^h_{rs,ik,l}
\end{aligned}\right\} \quad \ldots \quad (9)$$

Hiebei ist $y_{i(k)}$ kovariante Ableitung des Vektors $y_{(i)} = y_i = \dfrac{\partial y}{\partial t_i}$ bezüglich f_2, also:

$$y_{i(k)} = \frac{\partial y_i}{\partial t_k} - \Gamma^{\mu}_{ik} y_{\mu} = y_{ik} - \Gamma^{\mu}_{ik} y_{\mu}, \quad \ldots \ldots \quad (10)$$

wo

$$\Gamma^{\mu}_{ik} = g^{\mu\nu} \Gamma_{\nu,ik} = \tfrac{1}{2} g^{\mu\nu} \left(\frac{\partial g_{\nu i}}{\partial t_k} + \frac{\partial g_{\nu k}}{\partial t_i} - \frac{\partial g_{ik}}{\partial t_\nu} \right)$$

die 3-Indicessymbole zweiter Art sind.

Weiters ist

$$y_{i(k)(l)} = \frac{\partial y_{i(k)}}{\partial t_l} - \Gamma^{\mu}_{il} y_{\mu(k)} - \Gamma^{\mu}_{kl} y_{i(\mu)} \cdot \quad \ldots \ldots \quad (11)$$

y_i ist ein kovarianter Vektor, aber wegen

$$\tilde{y} = \lambda y \quad , \quad \tilde{y}_i = \lambda \tilde{y}_i + \lambda_i y$$

kein projektiver Vektor. Ebenso sind $y_{i(k)}$, $y_{i(k)(l)}$ wohl Tensoren, aber keine projektiven Tensoren.

Mit Hilfe der Gleichungen (10) and (11) sind die ψ_i von (9) eindeutig durch die φ_i von (5) und umgekehrt aus zu drücken.

Unsere Aufgabe ist jetzt zurückgebracht auf die folgende: aus den

Transformationsgleichungen der Funktionen ψ_i und deren Ableitungen sind die Ableitungen $\frac{\partial^s t}{\partial \overline{t}^s}$ zu eliminieren.

Wie verhalten sich nun die Funktionen ψ_i bei den Transformationen (6)? Wir haben

$$\overline{y} = y \ , \ \overline{y}_i = y_\mu \frac{\partial t_\mu}{\partial \overline{t}_i} \ , \ (\overline{y}_1 \ldots \overline{y}_m) = (y_1 \ldots y_m) \, . \, \triangle \ , \ \overline{A} = \triangle^{m+2} \, . \, A$$

und finden deshalb:

$$\overline{g}_{ik} = g_{\lambda\mu} \frac{\partial t_\lambda}{\partial \overline{t}_i} \ \frac{\partial t_\mu}{\partial \overline{t}_k}$$

$$\overline{\varphi}_{ik,rs} = \varphi_{\lambda\mu,\rho\sigma} \frac{\partial t_\lambda}{\partial \overline{t}_i} \ \frac{\partial t_\mu}{\partial \overline{t}_k} \ \frac{\partial t_\rho}{\partial \overline{t}_r} \ \frac{\partial t_\sigma}{\partial \overline{t}_s}$$

und analog bei ψ_4 und ψ_5. Bei ψ_3 und ψ_6 haben wir dagegen:

$$\overline{\alpha}^{h}_{ik,rs,} = \overset{\nu}{\alpha}_{\lambda\mu,\rho\sigma} \frac{\partial t_\lambda}{\partial \overline{t}_i} \ \frac{\partial t_\mu}{\partial \overline{t}_k} \ \frac{\partial t_\rho}{\partial \overline{t}_r} \ \frac{\partial t_\sigma}{\partial \overline{t}_s} \, . \, \frac{\partial \overline{t}_h}{\partial t_\nu}$$

$$\overline{\eta}^{h}_{rs,ik,l} = \overset{\nu}{\eta}_{\rho\sigma,\lambda\mu,\tau} \frac{\partial t_\rho}{\partial \overline{t}_r} \ \frac{\partial t_\sigma}{\partial \overline{t}_s} \ \frac{\partial t_\lambda}{\partial \overline{t}_i} \ \frac{\partial t_\mu}{\partial \overline{t}_k} \, . \, \frac{\partial \overline{t}_h}{\partial t_\nu}$$

Die Funktionen ψ_i sind daher selbst Tensorkomponenten und unser Problem ist jetzt auf die viel einfachere Frage zurückgeführt: aus den *Tensoren* (9) *und deren kovarianten Ableitungen sind Invarianten J aufzubauen, die auch bei den Transformationen* $\tilde{y} = \lambda y$ *die Invarianteneigenschaft besitzen.*

§ 3.

Ein besonderer Fall der Identität (2) ist gegeben durch:

$$\left.\begin{aligned} (y y_1 \ldots y_m y_{i(k)})\, y_{r(s)} = (y_{r(s)} y_1 \ldots y_m y_{i(k)})\, y - \Sigma\, (y_{r(s)} y_1 \ldots y \ldots y_m y_{i(k)})\, y_h \, + \\ + \, (y y_1 \ldots y_m y_{r(s)})\, y_{r(k)}. \end{aligned}\right\} \quad (12)$$

Teilen wir hier durch $\sqrt[m+2]{A}$, dann haben wir nach (9):

$$g_{ik}\, y_{r(s)} = \varphi_{ik,rs}\, y + \overset{h}{\alpha}_{ik,rs}\, y_h + g_{rs}\, y_{i(k)}. \quad \ldots\ldots \quad (13)$$

Hieraus folgt, wenn wir

$$Y = g^{rs} y_{r(s)} \quad \ldots\ldots\ldots\ldots \quad (14)$$

und

$$\overset{h}{\alpha}_{ik} = g^{rs} \overset{h}{\alpha}_{ik,rs} = (y_{i(k)} y_1 \ldots y \ldots y_m Y) \, . \, A^{-\frac{1}{m+2}} \quad \ldots\ldots \quad (15)$$

$$\varphi_{ik} = g^{rs} \varphi_{ik,rs} = (y_{i(k)} y_1 \ldots y_m Y) \, . \, A^{-\frac{1}{m+2}} \quad \ldots\ldots \quad (16)$$

setzen, wegen $g^{ik} g_{ik} = m$, die wichtige Beziehung [1]):

$$m y_{i(k)} = \varphi_{ik}\, y - \overset{h}{\alpha}_{ik}\, y_h + g_{ik}\, Y \quad \ldots\ldots\ldots \quad (17)$$

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[1]) G. FUBINI, l.c. § 5, (31).

Vermöge dieser Gleichung kann man die Tensoren (9) vereinfachen. Zunächst wird nämlich, wenn wird (17) in ψ_2 von (9) einsetzen:

$$\varphi_{ik,rs} = \varphi_{ik}\,(yy_1 \ldots y_m\, y_{r(s)}) \,.\, A^{-\frac{1}{m+2}} + g_{ik}\,(Yy_1 \ldots y \ldots y_m\, y_{r(s)}) \,.\, A^{-\frac{1}{m+2}},$$

also nach (16):

$$m\,\varphi_{ik,rs} = \varphi_{ik}\, g_{rs} - \varphi_{rs}\, g_{ik} \quad \ldots \ldots \ldots \quad (18)$$

In (9) können wir also $\varphi_{ik,rs}$ ersetzen durch φ_{ik}.

Bei ψ_3 von (9) erhält man auf dieselbe Weise:

$$m\,\overset{h}{\alpha}_{ik,rs} = \overset{h}{\alpha}_{ik}\, g_{rs} - \overset{h}{\alpha}_{rs}\, g_{ik} \quad \ldots \ldots \ldots \quad (19)$$

Bei ψ_5 haben wir:

$$m\,\vartheta_{rs,ik,l} = \varphi_{rs}\, h_{ik,l} + g_{rs}\,(Yy_1 \ldots y_m\, y_{i(k)(l)}) \,.\, A^{-\frac{1}{m+2}}$$

$$m\,\vartheta_{rs,ik,l} = \varphi_{rs}\, h_{ik,l} + g_{rs}\, \vartheta_{ik,l} \quad \ldots \ldots \ldots \quad (20)$$

wobei

$$\vartheta_{ik,l} = (Yy_1 \ldots y_m\, y_{i(k)(l)}) \,.\, A^{-\frac{1}{m+2}} = g^{rs}\,\vartheta_{rs,ik,l} \quad \ldots \quad (21)$$

gesetzt ist.

Schliesslich kommt bei ψ_6, wenn wir

$$\overset{h}{\eta}_{ik,l} = g^{rs}\,\overset{h}{\eta}_{rs,ik,l} = (Yy_1 \ldots y \ldots y_m\, y_{i(k)(l)}) \,.\, A^{-\frac{1}{m+2}} \quad \ldots \quad (22)$$

setzen:

$$m\,\overset{h}{\eta}_{rs,ik,l} = \overset{h}{\alpha}_{rs}\, h_{ik,l} + g_{rs}\,\overset{h}{\eta}_{ik,l} \quad \ldots \ldots \ldots \quad (23)$$

Also haben wir statt (9) die einfacheren Tensoren:

$$g_{ik}\ ,\ \varphi_{ik}\ ,\ \overset{h}{\alpha}_{ik}\ .\ h_{ik,l}\ ,\ \vartheta_{ik,l}\ ,\ \overset{h}{\eta}_{ik,l} \quad \ldots \ldots \ldots \quad (24)$$

§ 4.

Jetzt wollen wir zeigen, dass wir den gemischten Tensor α^h_{ik} in (24) weglassen können.

Wir haben:

$$g_{ik} = (yy_1 \ldots y_m\, y_{i(k)}) \,.\, A^{-\frac{1}{m+2}}.$$

Differentieren wir dies kovariant, dann wird vermöge

$$g_{ik\,(l)} = \frac{\partial g_{ik}}{\partial t_l} - \Gamma^h_{il}\, g_{hk} - \Gamma^h_{kl}\, g_{ik} \equiv 0:$$

$$\left\{ \sum_h (yy_1 \ldots y_{hl} \ldots y_m\, y_{i(k)}) + (yy_1 \ldots y_m\, y_{i(k)l}) - \frac{1}{m+2}\frac{A_l}{A}\,(yy_1 \ldots y_m\, y_{i(k)}) \right\} =$$

$$= [\Gamma_{k,il} + \Gamma_{i,kl}] \,.\, A^{\frac{1}{m+2}}$$

Setzen wir hier y_{hl} aus (10) und $y_{i(k)l} = \frac{\partial y_{i(k)}}{\partial t_l}$ aus (11) ein, dann erhalten wir wegen (9):

$$(-\alpha^{h}_{hl,ik} + g_{ik}\Gamma^{h}_{hl}) + (h_{ik,l} + g_{hk}\Gamma^{h}_{il} + g_{ih}\Gamma^{h}_{kl}) - \frac{1}{m+2}\frac{A_l}{A}\, g_{ik} = \Gamma_{k,il} + \Gamma_{i,kl},$$

also wegen

$$\Gamma^{h}_{hl} = \frac{1}{2}\frac{\partial \log g}{\partial t_l} = \frac{1}{2}\frac{\partial \log A^{\frac{2}{m+2}}}{\partial t_l} = \frac{1}{m+2}\frac{A_l}{A} \quad . \quad . \quad . \quad (25)$$

$$\alpha^{h}_{hl,ik} = \alpha^{\star}_{l,ik} = h_{ik,\,l} = (y y_1 \ldots y_m\, y_{i(k)(l)}) \,.\, A^{-\frac{1}{m+2}} \quad . \quad . \quad . \quad . \quad (26)$$

Dabei entsteht der Tensor $\alpha^{\star}_{l,ik}$ aus $\alpha^{h}_{rl,ik}$ durch Verjüngung.

Bei $\alpha^{\star}_{l,ik}$ und also auch bei $h_{ik,l}$ können wir das Komma zwischen *ik* und *l* weglassen. Nach der Identität van RICCI [1]) ist nämlich

$$y_{i(k)(l)} - y_{i(l)(k)} = R^{h}_{i,kl}\, y_h\,, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (27)$$

wo $R^{h}_{i,kl}$ der gemischte Krümmungstensor von g_{ik} ist. Nach (27) ist dann

$$(y y_1 \ldots y_m\, y_{i(k)(l)}) = (y y_1 \ldots y_m\, y_{i(l)(k)}),$$

also

$$h_{ik,l} = h_{ikl} = h_{kil} = h_{ilk} = \alpha^{\star}_{ikl} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (28)$$

ein symmetrischer Tensor dritter Stufe und das gleiche gilt nach (26) von $\alpha^{\star}_{l,ik}$.

Der Tensor h_{ikl} ist nichts anderes als die kubische Differentialform

$$F_3 = (m+2)\, A\, [3\, dF_2 - 2\, (v'\, d^3 y)] - 3\, F_2 \,.\, dA.$$

Führen wir nämlich hier die kovarianten Ableitungen $y_{i(k)}$ und $y_{i(k)(l)}$ an Stelle von y_{ik} und y_{ikl} ein, so wird wegen

$$\frac{dA}{A} = \frac{m+2}{2}\, g^{ik}\, dg_{ik}$$

$$h_{ikl}\, dt^i\, dt^k\, dt^l = -\frac{1}{2\,(m+2)}\, F_3 \,.\, A^{-\frac{1}{m+2}} \quad . \quad . \quad . \quad . \quad (29)$$

Der Tensor $\alpha^{h}_{ik,rs}$ ist nach (9) bezgl. *ik* und *rs* alternierend. Darum ist

$$\alpha^{s}_{ik,rs} = -\,\alpha^{s}_{rs,ik} = -\,\alpha^{s}_{sr,ik} = -h_{ikr} \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

und

$$\alpha^{\nu}_{ik,rs}\, g^{ik} g^{rs} = \alpha^{\nu}_{ik}\, g^{ik} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

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[1]) Vgl. z. B. mein Buch: Invariantentheorie, Groningen (1923), S. 345.

Setzen wir in (19) $i = h$, dann wird nach (26):

$$m h_{krs} = \overset{h}{\alpha}_{hk}\, g_{rs} - \overset{h}{\alpha}_{rs}\, g_{hk} = \alpha_k\, g_{rs} - \overset{h}{\alpha}_{rs}\, g_{hk} \quad \ldots\ldots \quad (32)$$

$$m h_{krs}\, g^{rs} = m \alpha_k - \overset{h}{\alpha}_{rs}\, g_{rs}\, g_{hk},$$

also

$$h_{krs}\, g^{rs} = \alpha_k = \overset{i}{\alpha}_{ik} \quad \ldots\ldots\ldots\ldots \quad (33)$$

Multiplizieren wir dagegen (32) mit g^{ks}, dann ist nach (33):

$$m h_{krs}\, g^{ks} = m \alpha_r = \alpha_k\, g_{rs}\, g^{ks} - \overset{h}{\alpha}_{rs}\, g_{hk}\, g^{ks} = \alpha_k\, \delta_r^k - \overset{h}{\alpha}_{rs}\, \delta_h^s = 0,$$

$$\alpha_l = h_{ikl}\, g^{ik} = \overset{i}{\alpha}_{il} = 0 \quad \ldots\ldots\ldots\ldots \quad (34)$$

Dies ist die bekannte Beziehung, die die Apolarität zwischen F_2 und F_3 ausdrückt.

(32) gibt dann wegen (34):

$$m h_{krs} = - \overset{h}{\alpha}_{rs}\, g_{hk}; \quad \ldots\ldots\ldots\ldots \quad (35)$$

daher ist nach (26):

$$m \overset{*}{\alpha}_{lik} = - \overset{h}{\alpha}_{ik}\, g_{hl}, \quad \ldots\ldots\ldots\ldots \quad (36)$$

d.h. das Herunterholen von h in α^h_{ik} gibt bis auf den Faktor $-m$ den Tensor $\overset{*}{\alpha}_{lik} = h_{lik}$. Daher ist auch

$$\overset{h}{\alpha}_{ik} = - m h_{ikl}\, g^{lh} = - m \overset{h}{h}_{ik}. \quad \ldots\ldots\ldots \quad (37)$$

und statt (17) kan man schreiben[1]):

$$m y_{i(k)} = \varphi_{ik} \cdot y + m h_{ikl}\, g^{l\nu} \cdot y_\nu + g_{ik} \cdot Y \quad \ldots\ldots \quad (38)$$

Hiedurch ist nun der Tensor $\alpha^h_{ik,rs}$ und alle aus ihm mittels $g_{\lambda\mu}$ und $g^{\lambda\mu}$ hergeleiteten Tensoren reduziert auf h_{ikl} und wir können also in (9) ψ_3, also in (24) α^h_{ik} weglassen.

§ 5.

Statt (24) haben wir also noch die fünf Tensoren:

$$\left.\begin{aligned}
g_{ik} &= (y y_1 \ldots y_m\, y_{i(k)} \cdot A^{-\frac{1}{m+2}} \\
\varphi_{ik} &= (y_{i(k)}\, y_1 \ldots y_m\, Y) \cdot A^{-\frac{1}{m+2}} \\
h_{ikl} &= (y y_1 \ldots y_m\, y_{i(k)(l)}) \cdot A^{-\frac{1}{m+2}} \\
\vartheta_{ik,l} &= (Y y_1 \ldots y_m\, y_{i(k)(l)}) \cdot A^{-\frac{1}{m+2}} \\
\overset{h}{\eta}_{ik,l} &= (Y y_1 \ldots y \ldots y_m\, y_{i(k)(l)}) \cdot A^{-\frac{1}{m+2}}
\end{aligned}\right\} \quad \ldots\ldots \quad (39)$$

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[1]) G. Fubini, Rend. Lincei V, 27 (1918), S. 147.

Wir untersuchen das Verhalten dieser Tensoren bei den Transformationen $\tilde{y} = \lambda y$. Wir haben

$$\tilde{y}_i = \lambda y_i + y \lambda_i$$

oder, wenn wir

$$\mu_i = \frac{\partial \log \lambda}{\partial t_i} = \frac{\lambda_i}{\lambda}$$

setzen:

$$\tilde{y}_i = \lambda (y_i + \mu_i y) \quad . \; . \; . \; . \; . \; . \; . \; . \; . \quad (40)$$

g_{ik} ist bereits ein projektiver Tensor:

$$\tilde{g}_{ik} = \lambda^2 g_{ik} \quad , \quad \tilde{g}^{ik} = \frac{1}{\lambda^2} g^{ik}.$$

Hieraus finden wir

$$\tilde{\Gamma}^{\nu}_{ik} = \Gamma^{\nu}_{ik} + \delta^{\nu}_{i} \mu_k + \delta^{\nu}_{k} \mu_i - g_{ik} \mu^{\nu} \qquad (\mu^{\nu} = g^{\nu s} \mu_s) \quad . \; . \; . \quad (41)$$

Weiter aus (40):

$$\tilde{y}_{ik} = \lambda [y_{ik} + y_i \mu_k + y_k \mu_i + y (\mu_{ik} + \mu_i \mu_k) \qquad \left(\mu_{ik} = \frac{\partial \mu_i}{\partial t_k}\right) . \quad . \quad (42)$$

$$\tilde{y}_{i(k)} = \frac{\partial \tilde{y}_i}{\partial t_k} - \tilde{\Gamma}^{\nu}_{ik} \tilde{y}_{\nu}$$

$$\tilde{y}_{i(k)} = \lambda [y_{i(k)} + g_{ik} \mu^{\rho} \mu_{\rho} + y (\mu_{ik} - \Gamma^{\rho}_{ik} \mu_{\rho} + g_{ik} \mu - \mu_i \mu_k)] \quad (\mu = \mu^{\rho} \mu_{\rho}) \quad (43)$$

$$\tilde{Y} = \tilde{g}^{ik} \tilde{y}_{i(k)} = \frac{1}{\lambda} [Y + m \mu^{\rho} y_{\rho} + y (g^{ik} \mu_{i(k)} + (m-1) \mu)] \quad . \quad (44)$$

Um aus diesen Transformationsgleichungen μ_i und μ_{ik} eliminieren zu können, benötigen wir eine Invariante M mit $\triangle$-Gewicht Null und λ-Gewicht eins[1]). Ist nämlich

$$\overline{M} = \mathrm{M} \quad , \quad \overset{\frown}{M} = \lambda^n . M,$$

dann erhalten wir analog zu (43):

$$\overset{\frown}{M}_{i(k)} = \lambda^n . [M_{i(k)} + g_{ik} M^{\rho} \mu_{\rho} + (n-1)(M_i \mu_k + M_k \mu_i) +$$
$$+ n M (\mu_{i(k)} + g_{ik} \mu + (n-2) \mu_i \mu_k)]$$

also bei $n = 1$:

$$\overset{\frown}{M}_{i(k)} = \lambda [M_{i(k)} + g_{ik} M^{\rho} \mu_{\rho} + M (\mu_{i(k)} + g_{ik} \mu - \mu_i \mu_k)] \quad . \quad . \quad (45)$$

Nach (43) und (45) wird somit:

$$\overset{\frown}{M} \tilde{y}_{i(k)} - \tilde{y} \overset{\frown}{M}_{i(k)} = \lambda^2 [M y_{i(k)} - y M_{i(k)} + M g_{ik} \mu^{\rho} y_{\rho} - y g_{ik} M^{\rho} y_{\rho}].$$

Wegen

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[1]) Es ist dabei gleichgültig, wie diese Invariant M entsteht.

$$\mu_\rho = \frac{\overset{\frown}{M}_\rho}{\overset{\frown}{M}} - \frac{M_\rho}{M} \quad , \quad \overset{\frown}{M} \tilde{y}_\sigma - \tilde{y} \overset{\frown}{M}_\sigma = \lambda^2 (M y_\sigma - y M_\sigma$$

folgt daher, dass

$$M y_{i(k)} - g_{ik} M^\rho y_\rho + y \left(g_{ik} \frac{M^\rho M_\rho}{M} - M_{i(k)} \right) \quad . \quad . \quad (46)$$

ein *projektiver* Tensor mit λ-Gewicht 2 ist.

Hieraus finden wir die absolute projektive Invariante

$$Z = MY - mM^\rho y_\rho + y \left(m \frac{M^\rho M_\rho}{M} - g^{ik} M_{i(k)} \right) . \quad . \quad . \quad (47)$$

Auch der Tensor h_{ikl} ist bereits projektiv und hat das λ-Gewicht 2:

$$\tilde{h}_{ikl} = \lambda^2 h_{ikl}.$$

Bei φ_{ik} haben wir nach (39), (43), (44) und

$$(v' Y) = (y y_1 \ldots y_m Y) = m \, . \, A^{\frac{1}{m+2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (48)$$

$$(y_{i(k)} y_1 \ldots y \ldots y_m Y) = \overset{h}{a}_{ik} \, . \, A^{\frac{1}{m+2}} \quad . \quad . \quad . \quad . \quad . \quad . \quad (49)$$

$$\varphi_{ik} = \varphi_{ik} - g_{ik} (g^{rs} \mu_{r(s)} + (m-1) \mu) + m (\mu_{i(k)} + g_{ik} \mu - \mu_i \mu_k) + \overset{h}{a}_{ik} \mu_h \, . \quad (50)$$

Hier können wir nun nach (45) und

$$\tilde{g}^{rs} \overset{\frown}{M}_{r(s)} = \frac{1}{\lambda} [g^{rs} M_{r(s)} + mM^\rho \mu_\rho + M (g^{rs} \mu_{r(s)} + (m-1) \mu)] \quad . \quad (51)$$

die Ausdrücke zwischen den Klammern eliminieren ($g^{rs} M_{r(s)}$ ist der "zweite Differentialparameter" $\triangle_2 M$ von M). Wir erhalten so den projektiven Tensor

$$f_{ik} = M \varphi_{ik} - mM_{i(k)} + g_{ik} g^{rs} M_{r(s)} - \overset{v}{a}_{ik} M_v \quad . \quad . \quad . \quad . \quad (52)$$

$$\tilde{f}_{ik} = \lambda \, . \, f_{ik} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (53)$$

Dieser projektive Tensor kommt also an die Stelle des (nicht-projektiven) Tensors φ_{ik}. Wie man aus (52) ablesen kann, ist

$$f_{ik} g^{ik} = 0 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (54)$$

Die zweite quadratische Differentialform $f_{ik} \, dt^i \, dt^k$ ist also mit g_{ik} apolar. Benützen wir (37), dann haben wir statt (52) auch:

$$f_{ik} = M \varphi_{ik} - mM_{i(k)} + g_{ik} g^{rs} M_{r(s)} + mh_{ikl} M^l \quad . \quad . \quad . \quad (55)$$

Ist $M = 1$, so wird $f_{ik} = \varphi_{ik}$ und nach (47) $Z = Y$. Setzt man $\overset{\frown}{M} = 1$ in $\overset{\frown}{M} = \lambda M$, also

$$\lambda = \frac{1}{M}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (56)$$

dann sind $\tilde{y} = \lambda y = \frac{y}{M}$ Normalkoordinaten, analog mit den projektiven Normalkoordinaten von FUBINI.

Die grundlegende Gleichung (38) kann nach (55) wie folgt geschrieben worden:

$$mMy_{i(k)}=y(f_{ik}+mM_{i(k)}-g_{ik}g^{rs}M_{r(s)}-mh_{ikl}M^{l})+mMh_{ikl}g^{l\nu}y_{\nu}+Mg_{ik}Y \quad (57)$$

Drücken wir hier noch MY nach (47) durch Z aus, so bekommen wir:

$$\left.\begin{aligned} mMy_{i(k)}=y\left(f_{ik}+mM_{i(k)}-mg_{ik}\frac{M^{\rho}M_{\rho}}{M}-mh_{ikl}M^{l}\right)+ \\ +m(Mh^{\nu}_{ik}+M^{\nu}g_{ik})\,y_{\nu}+g_{ik}Z. \end{aligned}\right\} \quad . \quad (58)$$

§ 6.

Statt (58) schreiben wir kürzer

$$mMy_{i(k)}=yp_{ik}+q^{\nu}_{ik}y_{\nu}+g_{ik}Z, \quad \ldots\ldots \quad (59)$$

setzen also:

$$p_{ik}=f_{ik}+mM_{i(k)}-mg_{ik}\frac{M^{\rho}M_{\rho}}{M}-mh_{ikl}M^{l} \quad \ldots \quad (60)$$

$$q^{\nu}_{ik}=m(Mh^{\nu}_{ik}+g_{ik}M^{\nu}) \quad \ldots\ldots\ldots \quad (61)$$

Differenzieren wir (38) kovariant nach t_l so wird:

$$my_{i(k)(l)}=y\,\varphi_{ik(l)}+y_l\,\varphi_{ik}+mh^{\nu}_{ik(l)}\,y_{\nu}+mh^{\nu}_{ik}\,y_{h(l)}+g_{ik}Y_l \quad \ldots \quad (62)$$

Setzen wir dies nun in $\vartheta_{ik,l}$ und $\eta^{\nu}_{ik,l}$ (vgl. (39)) ein, dann sehen wir, dass sich diese Tensoren durch g_{ik}, φ_{ik}, h_{ikl} und die zwei folgenden

$$(y_{i(k)}\,y_1\ldots y_m\,Y_l)\,.\,A^{-\frac{1}{m+2}} \quad , \quad (y_{i(k)}\,y_1\ldots y\ldots y_m\,Y_l)\,.\,A^{-\frac{1}{m+2}}$$

ausdrücken lassen. In diesen beiden können wir nach (47) Z statt Y einführen und bekommen als neue Tensoren die folgenden:

$$\varrho_{ik,l}=(y_{i(k)}\,y_1\ldots y_m\,Z_l)\,.\,A^{-\frac{1}{m+2}} \quad , \quad \varepsilon^{\nu}_{ik,l}=(y_{i(k)}\,y_1\ldots y\ldots y_m\,Z_l)\,.\,A^{-\frac{1}{m+2}}. \quad (63)$$

Statt (24) haben wir jetzt

$$g_{ik} \quad , \quad f_{ik} \quad , \quad h_{ikl} \quad , \quad \varrho_{ik,l} \quad , \quad \varepsilon^{\nu}_{ik,l} \quad \ldots\ldots \quad (64)$$

Nach (48) und (47) finden wir

$$(v'Z)=(yy_1\ldots y_m Z)=mM\,.\,A^{\frac{1}{m+2}}. \quad \ldots\ldots \quad (65)$$

Hieraus folgt nach (47), (10), (25) und (34):

$$(v'Z_l)=0 \quad \ldots\ldots\ldots\ldots \quad (66)$$

Berechnen wir nun $\tilde{\varepsilon}^{\nu}_{ik,l}$, dann bekommen wir nach (66) und wegen $\tilde{Z}=Z, \tilde{Z}_i=Z_i$:

$$\tilde{\overset{\nu}{\varepsilon}}_{ik,l} = \lambda \,.\, \overset{\nu}{\varepsilon}_{ik,l} \quad \ldots\ldots\ldots\ldots \quad (67)$$

d.h. $\tilde{\overset{\nu}{\varepsilon}}_{ik,l}$ ist bereits ein *projektiver* Tensor.

Bei $\varrho_{ik,l}$ dagegen haben wir

$$\tilde{\varrho}_{ik,l} = \lambda\, \varrho_{ik,l} + \overset{\nu}{\varepsilon}_{ik,l}\, \mu_\nu \,.$$

Ist nun wieder N eine projektive Differentialinvariante mit $\triangle$-Gewicht Null und λ-Gewicht 1, dann haben wir, so wie oben bei der Invariante M (man könnte auch $M = N$ nehmen):

$$\mu_\nu = \frac{\tilde{N}_\nu}{\tilde{N}} - \frac{N_\nu}{N} \,.$$

Also ist nicht $\varrho_{ik,l}$ selbst, sondern

$$\sigma_{ik,l} = \varrho_{ik,l} - \overset{\nu}{\varepsilon}_{ik,l} \frac{N_\nu}{N} \quad \ldots\ldots\ldots\ldots \quad (68)$$

ein *projectiver* Tensor.

Nun können wir $\sigma_{ik,l}$ und $\overset{h}{\varepsilon}_{ik,l}$ mit Hilfe von (38) noch vereinfachen.

Drücken wir $y_{i(k)}$ in $(y_{i(k)}\, y_1 \ldots y \ldots y_m Z_l)$ nach (38) aus, dann haben wir nach (63) und (66):

$$\overset{\nu}{\varepsilon}_{ik,l} = \frac{1}{m}\, g_{ik}\, (Y y_1 \ldots y \ldots y_m Z_l) \,.\, A^{-\frac{1}{m+2}}$$

$$\overset{\nu}{\varepsilon}_{ik,l} = \frac{1}{m}\, g_{ik}\, g^{rs}\, \overset{\nu}{\varepsilon}_{rs,l} = \frac{1}{m}\, g_{ik}\, \overset{\nu}{\varepsilon}_l \quad \ldots\ldots\ldots\ldots \quad (69)$$

Statt $\varepsilon^{\nu}_{ik,l}$ haben wir also jetzt den projektiven Tensor

$$\overset{\nu}{\varepsilon}_l = (Y y_1 \ldots y \ldots y_m Z_l) \,.\, A^{-\frac{1}{m+2}} \quad \ldots\ldots \quad (70)$$

Bei $\varrho_{ik,l}$ finden wir auf dieselbe Art:

$$\varrho_{ik,l} = \frac{1}{m}\, g_{ik}\, (Y y_1 \ldots y_m Z_l) \,.\, A^{-\frac{1}{m+2}}$$

$$= \frac{1}{m}\, g_{ik}\, g^{rs}\, \varrho_{rs,l} = \frac{1}{m}\, g_{ik}\, \varrho_l \,.$$

Also kommt statt (68):

$$\sigma_l = \varrho_l - \overset{\nu}{\varepsilon}_l \frac{N_\nu}{N} \quad \ldots\ldots\ldots\ldots \quad (71)$$

wo

$$\sigma_l = (Y y_1 \ldots y_m Z_l) \,.\, A^{-\frac{1}{m+2}} \quad \ldots\ldots\ldots \quad (72)$$

Daher haben wir schliesslich statt (64) die *projektiven* Tensoren:

$$g_{ik} \;,\; f_{ik} \;,\; h_{ikl} \;,\; \sigma_l \;,\; \overset{\nu}{\varepsilon}_l \quad \ldots\ldots \quad (73)$$

Hierbei sind die Tensoren f_{ik} und ε^{ν}_l mit Hilfe der Invariante M, dagegen der Tensor σ_l mit Hilfe der Invarianten M und N hergeleitet. Die Reduktion der beiden letzten Tensoren σ_l und ε^{ν}_l soll den Gegenstand einer folgenden Mitteilung bilden.

Chemistry. — *"Equilibria in systems, in which phases, separated by a semipermeable membrane.* VI. By F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of February 28, 1925).

In the previous communications we have discussed some simple cases of osmose in binary and ternary systems. We now shall deduce some general properties.

The osmotic water-attraction of a system of phases.

In our previous considerations we have discussed already the O.W.A. of a liquid and in some simple cases also that of one or more solid substances; now we shall consider more general cases. We take the osmotic equilibrium:

$$E = [E_1\,(n_1\,r_1) \,\vert\, E_2\,(n_2\,r_2) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

in which E_1 is a system of n_1 components in r_1 phases under the pressure P_1 and E_2 a system of n_2 components in r_2 phases under the pressure P_2.

We now imagine that a small quantity of water (in general: of the diffusing substance) passes from the system E_2 into the system E_1; then the thermodynamical potential of the system E_1 will change with δZ_1, that of the system E_2 with δZ_2. When $\delta Z_1 + \delta Z_2 = 0$, then system (1) is in equilibrium, when $\delta Z_1 + \delta Z_2 < 0$, then water will diffuse through the membrane. In order to define the direction, in which the water will diffuse through the membrane, we have to know δZ_1 and δZ_2. Firstly we shall define δZ_1 for the system E_1; for this we distinguish different cases.

I. The system E_1 consists of a liquid only.

We call the n_1 components, of which the liquid L_1 consists, $XY \ldots W$; we represent the composition of the liquid by:

$$x_1\,Mol\,X + y_1\,Mol\,Y \ldots + (1 - x_1 - y_1 \ldots)\,Mol\,W.$$

We assume that there are q_1 quantities of this liquid L_1, each with the thermodynamical potential ζ_1. When a small quantity μ of the diffusing substance W passes from the system E_2 into those q_1 quantities of the liquid L_1, then follows:

$$\delta Z_1 = (q_1 + \mu)\left(\zeta_1 + \frac{\partial \zeta_1}{\partial x_1}\,dx_1 + \frac{\partial \zeta_1}{\partial y_1}\,dy_1 \ldots \right) - q_1 \zeta_1 .$$

As, when μ is infinitely small with respect to q,

$$dx_1 = \frac{q_1 x_1}{q_1 + \mu} - x_1 = -\frac{\mu}{q_1} x_1 \qquad dy_1 = \frac{q_1 y_1}{q_1 + \mu} - y_1 = -\frac{\mu}{q_1} y_1$$

etc. we may write also:

$$\delta Z_1 = \left(\zeta_1 - x_1 \frac{\partial \zeta_1}{\partial x_1} - y_1 \frac{\partial \zeta_1}{\partial y_1} - \dots \right) \mu = \varphi_1 \mu \quad . \quad . \quad . \quad (2)$$

Previously we have seen that the value of φ_1 in connection with a corresponding value of the system E_2 decides whether the substance W will diffuse from the liquid L_1 towards the system E_2 or reversally; for the sake of abbreviation we shall say therefore that φ_1 defines the O.W.A. of the liquid L_1.

II. *The system E_1 consists of two or more liquids.*

When two or more liquids are in equilibrium with one another, then they are isotonic with respect to all components; consequently they also have the same O.W.A. It is obvious, therefore, also that the O.W.A. of a complex of liquids is equal to the O.W.A. of each of them, separately. We are able to prove this still also in the following way. For the sake of simplicity we take a system of two liquids viz.

$$E_1 = L_1 + L_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

We represent the composition of

L_1 by x_1 *Mol* $X + y_1$ *Mol* $Y \dots + (1 - x_1 - y_1 \dots)$ *Mol* W
L_2 by x_2 *Mol* $X + y_2$ *Mol* $Y \dots + (1 - x_2 - y_2 \dots)$ *Mol* W.

We take q_1 quantities of L_1 and q_2 quantities of L_2, each with the thermodynamical potential ζ_1 and ζ_2. We now imagine that a small quantity μ of the diffusing substance W passes from the system E_2 into the system E_1. When α_1 quantities of W go towards the q_1 quantities of L_1 and α_2 quantities of W towards the q_2 quantities of L_2, then is, therefore $\alpha_1 + \alpha_2 = \mu$. Further we assume that at the same time $\delta n_x \, \delta n_y \dots \delta n_w$ quantities of the substances $X \, Y \dots W$ pass from the q_2 quantities of L_2 into the q_1 quantities of L_1. We now have:

$$\delta Z_1 = (q_1 + \triangle + \alpha_1) \left(\zeta + \frac{\partial \zeta}{\partial x} dx + \frac{\partial \zeta}{\partial y} dy \dots \right)_1 \quad . \quad . \quad . \quad (4)$$

$$+ (q_2 - \triangle + \alpha_2) \left(\zeta + \frac{\partial \zeta}{\partial x} dx + \frac{\partial \zeta}{\partial y} dy \dots \right)_2 - q_1 \zeta_1 - q_2 \zeta_2$$

in which $\triangle = \delta n_x + \delta n_y \dots + \delta n_w$.

Further we find:

$$q_1 dx_1 = \delta n_x - x_1 (\triangle + \alpha_1) \qquad q_2 dx_2 = -\delta n_x + x_2 (\triangle - \alpha_2)$$

$$q_1 dy_1 = \delta n_y - y_1 (\triangle + \alpha_1) \qquad q_2 dy_2 = -\delta n_y + y_2 (\triangle - \alpha_2)$$

etc. With the aid of this (3) passes into:

$$\delta Z_1 = (\varphi_1 - \varphi_1)\,\Delta + \left(\frac{\partial \zeta_1}{\partial x_1} - \frac{\partial \zeta_2}{\partial x_2}\right)\delta n_x + \left(\frac{\partial \zeta_1}{\partial y_1} - \frac{\partial \zeta_2}{\partial y_2}\right)\delta n_y + \varphi_1\,\alpha_1 + \varphi_2\,\alpha_2 \quad (5)$$

in which:

$$\varphi_1 = \zeta_1 - x_1 \frac{\partial \zeta_1}{\partial x_1} - y_1 \frac{\partial \zeta_1}{\partial y_1} \dots$$

$$\varphi_2 = \zeta_2 - x_2 \frac{\partial \zeta_2}{\partial x_2} - y_2 \frac{\partial \zeta_2}{\partial y_2} \dots$$

We now imagine firstly the system (3) by itself so that $\alpha_1 = 0$ and $\alpha_2 = 0$. Then follow from (5) the known equations for equilibrium:

$$\varphi_1 = \varphi_2 \qquad \frac{\partial \zeta_1}{\partial x_1} = \frac{\partial \zeta_2}{\partial x_2} \qquad \frac{\partial \zeta_1}{\partial y_1} = \frac{\partial \zeta_2}{\partial y_2} \text{ etc.} \quad \dots\dots \quad (6)$$

When now, as is assumed above, $\mu = \alpha_1 + \alpha_2$ quantities of W diffuse from E_2 towards the two liquids and when we assume that both these liquids are in equilibrium with one another, then (5) passes, therefore, into:

$$\delta Z_1 = \varphi_1\,\alpha_1 + \varphi_2\,\alpha_2 = \varphi_1\,\mu = \varphi_2\,\mu. \quad \dots\dots \quad (7)$$

Consequently it is apparent from this, as is already said above, that the O.W.A. of liquid L_1 is equal to that of L_2 and equal to that of the complex $L_1 + L_2$.

III. *The system E_1 contains, besides one or more liquids, still other phases.*

In the examples, discussed already formerly, we have seen that the O.W.A. of a binary or ternary liquid, which is saturated with a solid substance, is equal to the O.W.A. of the liquid only. Consequently the O.W.A. of a liquid does not change by the presence of a solid substance, with which it is in equilibrium. Generally this is the case. Let us take f. i. the system:

$$E_1 = L_1 + L_2 \dots + F_1 + F_2 + \dots$$

in which L_1, L_2 etc. represent liquids and F_1 $F_2 \dots$ other phases. Then the O.W.A. of L_1 is equal to that of L_2 etc. and equal to that of the total system E_1.

In order to show this for a system

$$E_1 = L + F_1 + F_2 \dots + F_{r-1} \quad \dots\dots \quad (8)$$

we represent the composition of

L by x *Mol* $X + y$ *Mol* $Y \dots + (1 - x - y \dots)$ *Mol* W

F_1 „ α_1 *Mol* $X + \beta_1$ *Mol* $Y \dots + (1 - \alpha_1 - \beta_1 \dots)$ *Mol* W

F_2 „ α_2 *Mol* $X + \beta_2$ *Mol* $Y \dots + (1 - \alpha_2 - \beta_2 \dots)$ *Mol* W

etc.; we call the thermodynamical potentials ζ ζ_1 ζ_2 etc.

We now imagine that a small quantity μ of the diffusing substance

W passes from a system E_2 into the system E_1; this will cause also that $\delta n_1\, \delta n_2 \ldots$ quantities of the phases $F_1\, F_2 \ldots$ pass into the liquid L. The change of the thermodynamical potential of the system E then is:

$$\left.\begin{aligned}\delta Z_1 = (q + \triangle + \mu)\left(\zeta + \frac{\partial \zeta}{\partial x}dx + \frac{\partial \zeta}{\partial y}dy \ldots\right) \\ - q\zeta - \zeta_1\,\delta n_1 - \zeta_2\,\delta n_2 \ldots\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (9)$$

in which: $\triangle = \delta n_1 + \delta n_2 \ldots + \delta n_{r-1}$. Further is assumed that in the equilibrium (8) q quantities of liquid occur. When we represent the quantities of the components $X\, Y \ldots W$, which pass into the liquid, by $\delta n_x\, \delta n_y \ldots \delta n_w$, then they are defined by:

$$\left.\begin{aligned}\delta n_x = \alpha_1\,\delta n_1 + \alpha_2\,\delta n_2 + \alpha_3\,\delta n_3 \ldots \\ \delta n_y = \beta_1\,\delta n_1 + \beta_2\,\delta n_2 + \beta_3\,\delta n_3 \ldots\end{aligned}\right\} \quad . \quad . \quad . \quad . \quad (10)$$

etc. Hence follows the relation:

$$\delta n_x + \delta n_y \ldots + \delta n_w = \triangle + \mu.$$

Now we find for the values, which we have to give to $dx\, dy \ldots$ in (9):

$$q \,.\, dx = \delta n_x - x\,(\triangle + \mu)$$

$$q \,.\, \delta y = \delta n_y - y\,(\triangle + \mu)$$

etc. With the aid of this (9) passes into:

$$\left.\begin{aligned}\delta Z_1 = \left(\zeta - x\frac{\partial \zeta}{\partial x} - y\frac{\partial \zeta}{\partial y} \ldots\right)(\triangle + \mu) - \zeta_1\,\delta n_1 - \zeta_2\,\delta n_2 \ldots \\ + \frac{\partial \zeta}{\partial x} \,.\, \delta n_x + \frac{\partial \zeta}{\partial y} \,.\, \delta n_y \ldots\end{aligned}\right\} \quad . \quad (11)$$

If we imagine in (11) the values of $\delta n_x\, \delta n_y \ldots$ from (10), to be substituted then it appears that (11) contains besides μ still the $r-1$ variations $\delta n_1\, \delta n_2 \ldots$

Firstly we take the system (8) by itself, so that $\mu = 0$. Then follow from (11) the known $r-1$ equations for equilibrium

$$\zeta - \zeta_i + (\alpha_i - x)\frac{\partial \zeta}{\partial x} + (\beta_i - y)\frac{\partial \zeta}{\partial y} + \ldots = 0 \quad . \quad . \quad . \quad (12)$$

$$i = 1,\ 2, \ldots (r - 1)$$

When, as is assumed above, μ quantities of the substance W diffuse towards the system E_1 and when we assume that this system is in equilibrium, then (11) passes into:

$$\delta Z_1 = \left(\zeta - x\frac{\partial \zeta}{\partial x} - y\frac{\partial \zeta}{\partial y} \ldots\right)\mu \quad . \quad . \quad . \quad . \quad . \quad (13)$$

The O.W.A. of the whole system (8) is the same, therefore, as that of the liquid.

Of course the considerations above are also true, when one of the solid phases is the diffusing substance W.

IV. *The system E_1 consists of solid substances only.*

We take a system:

$$E_1\,(n\,.\,r) = F_1 + F_2 \ldots + F_r \quad \ldots \ldots \ldots \quad (14)$$

of n components in r phases, we represent the composition of a phase F_i by:

$$\alpha_i \; Mol \; X + \beta_i \; Mol \; Y \ldots + (1 - \alpha_i - \beta_i \ldots) \; Mol \; W$$

$$i = 1, 2, \ldots, r$$

We assume that those solid phases have a constant composition. We now may distinguish several cases, according to the fact whether from system (14) by acceptance or loss of a small quantity of the diffusing substance W a liquid arises or not.

1°. *A liquid arises.*

When we take a system as f. i.

$$NaCl + NaNO_3 + Na_2SO_4$$

of course this cannot lose water but it can take in water.

In the latter case it passes into:

$$L + NaCl + NaNO_3 + Na_2SO_4$$

in which L is a liquid saturated with the solid substances. However, there are also systems which can form a liquid, also with loss of water.

A simple example is a. o. the hydrate $Fe_2\,Cl_6\,.\,12H_2O$ f.i. at 30°; this passes, when we witdraw from it a little water, into the equilibrium $L + Fe_2\,Cl_6\,.\,12\,H_2O$, in which the liquid L contains more Fe_2Cl_6 than the hydrate. Consequently we distinguish two cases.

a. The liquid is formed, when the system takes the diffusing substance.

In the previous communication we have put in some simple cases of ternary systems the O.W.A. of one or two solid substances equal to that of the liquid, which arises at the acceptance of a small quantity of water. That this is generally the case, appears a. o. in the following way. We assume that system (14) by acceptance of a small quantity of the diffusing substance W passes into the system:

$$L + F_1 + F_2 \ldots + F_r \quad \ldots \ldots \ldots \quad (15)$$

We give to L the composition:

$$x \; Mol \; X + y \; Mol \; Y \ldots + (1 - x - y \ldots) \; Mol \; W.$$

When this liquid arises by the liquefaction of δn_1 quantities of $F_1 + \delta n_2$ quantities of F_2 etc., with μ quantities of W, then we have:

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$$x=\frac{\alpha_1\,\delta n_1+\alpha_2\,\delta n_2\ldots}{\Delta+\mu}\quad;\quad y=\frac{\beta_1\,\delta n_1+\beta_2\,\delta n_2\ldots}{\Delta+\mu};\quad\ldots\quad(16)$$

etc. in which

$$\Delta=\delta n_1+\delta n_2\ldots+\delta n_r\,.$$

The change of the thermodynamical potential then is:

$$\delta Z_1=\zeta\,(\Delta+\mu)-\zeta_1\,\delta n_1-\zeta_2\,\delta n_2\quad\ldots\ldots\quad(17)$$

When we assume that system (15) is in equilibrium, then r equations of the form (12) are valid for this. With the aid of those and of (16) we find:

$$\zeta\,.\,\Delta+\left(x\frac{\partial\zeta}{\partial x}+y\frac{\partial\zeta}{\partial y}+\ldots\right)\mu-\zeta_1\,\delta n_1-\zeta_2\,\delta n_2\ldots=0$$

so that (17) passes into:

$$\delta Z_1=\left(\zeta-x\frac{\partial\zeta}{\partial x}-y\frac{\partial\zeta}{\partial y}-\ldots\right)\mu\quad\ldots\ldots\quad(18)$$

Hence follows that the O.W.A. of a system of solid phases is equal to the O.W.A. of the liquid, which arises when the system takes a little of the diffusing substance.

b. The liquid is formed, when the system loses the diffusing substance.

We now find the same as in case *a*. By recapitulation of both cases, it follows:

when in a system of solid substances a liquid L_1 is formed with acceptance of the diffusing substance W and a liquid L_2 is formed with loss of this substance W, then the O. W. A. of this system has two values; the one is equal to that of liquid L_1 and is valid for the acceptance, the other to that of liquid L_2 and is valid for the loss of the diffusing substance.

In the previous communications we have discussed already some simple examples.

2. *Two or more liquids arise,*

After the former considerations it is not necessary to discuss this case more in detail.

3. *No liquid arises.*

When a system E_1 of solid substances takes a little of the diffusing substance W f.i. water and no liquid is formed, then this taken water must be held in any way by the solid substances, or it must be deposited like ice or it must occur as watervapour. Let us take f.i. the system:

$$E_1=Na_2\,SO_4\quad\ldots\ldots\ldots\quad(19)$$

which consists of one substance only; this may pass by acceptance of water into the system:

$$E_1=Na_2\,SO_4+Na_2\,SO_4\,.\,10\,H_2O\quad\ldots\ldots\quad(20)$$

The system

$$E_1 = Fe_2Cl_6 . 7\,H_2O \quad . \; . \; . \; . \; . \; . \; . \; . \quad (21)$$

may pass into:

$$E_1 = Fe_2Cl_6 . 7\,H_2O + Fe_2Cl_6 . 12\,H_2O \quad . \; . \; . \; . \quad (22)$$

and the system:

$$E_1 = BaCl_2 . 2\,H_2O + HgCl_2 \quad . \; . \; . \; . \; . \quad (23)$$

below 17°.2 into the system:

$$E_1 = BaCl_2 . 2\,H_2O + HgCl_2 + BaCl_2 . 3\,HgCl_2 . 6\,H_2O \quad . \quad (24)$$

We represent the reactions occurring in those systems by

$$\left.\begin{array}{l} Na_2SO_4 - Na_2SO_4 . 10\,H_2O + 10 . H_2O = 0 \\ Fe_2Cl_6 . 7\,H_2O - Fe_2Cl_6 . 12\,H_2O + 5\,H_2O = 0 \\ BaCl_2 . 2\,H_2O + 3\,HgCl_2 - BaCl_2 . 3\,Hg\,Cl_2 . 6\,H_2O + 4\,H_2O = 0 \end{array}\right\} \quad (25)$$

From the systems 19, 21 and 23 a new phase arises, therefore, by acceptance of water; this is no more the case in the systems 20, 22 and 24 which have originated from those; only the quantities of the phases, which are present already, change in them. The same is true also, when we withdraw a little water from those systems 20, 22 and 24. Consequently we may say that in those systems at acceptance or loss of water a phases-reaction occurs, as is represented in (25), viz. a reaction, at which not the composition but only the quantity of the phases changes. As the systems 19, 21 and 23 by acceptance of a very small quantity of water pass at once already into 20, 22 and 24, we shall consider the latter only, consequently systems, in which at acceptance or loss of the diffusing substance a phases-reaction occurs.

We now take a similar system:

$$E_1 = F_1 + F_2 \ldots + F_r \quad . \; . \; . \; . \; . \; . \; . \; . \quad (26)$$

we represent the reaction, when μ quantities of the diffusing substance W are taken in by:

$$\lambda_1 F_1 + \lambda_2 F_2 + \ldots + \lambda_r F_r + \mu W = 0. \quad . \; . \; . \; . \quad (27)$$

In this [compare the reactions 25] some of the reaction-coefficients are positive, and other ones negative. Of course it may be also the case that one or more of the phases of (26) do not participate in the reaction [1]), the corresponding reaction-coefficients in 27 are zero then. A simple case we have f.i. in the system:

$$E_1 = \text{ice} + F_2 + F_3 \ldots + F_r \quad . \; . \; . \; . \; . \; . \; . \quad (28)$$

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[1]) Then we have a singular equilibrium. Compare for this: F. A. H. SCHREINEMAKERS: In-, mono- and plurivariants equilibria. XXVII and XXVIII.

when water is the diffusing substance. Reaction (27) then becomes:

$$-\mu \text{ quantities of ice} + \mu \text{ quantities of water} = 0 \quad . \quad . \quad . \quad (29)$$

or in the ordinary form: water ⇄ ice.

When system 26 takes in μ quantities of the diffusing substance W, then is the change of the thermodynamical potential:

$$\delta Z_1 = -\lambda_1 \zeta_1 - \lambda_2 \zeta_2 \ldots - \lambda_r \zeta_r \quad . \quad . \quad . \quad . \quad . \quad . \quad (30)$$

As viz. the quantity of a phase decreases when this is negative [compare f. i. the reactions 25], we must give in 30 the negative sign to $\lambda_1 \; \lambda_2 \ldots$

We now take a liquid L which is in equilibrium with the system 26. This is always possible. Let us take f. i. the system $Na_2SO_4 + Na_2SO_4 . 10 H_2O$ at a definite temperature T_1 and under a definite pressure P_1 and let us consider the system:

$$Na_2SO_4 + Na_2SO_4 . 10\, H_2O + L$$

at the same T_1 and P_1. Then we have three phases, while T_1 and P_1 are given; consequently the liquid must contain three components at least. When it contains three components, then its composition is completely defined; when it contains four components, then it is represented by the points of a curve in space; etc.

When we take the system with the two ternary double-salts. $D . \alpha\, H_2O + D \beta . H_2O$, so that in this a phases-reaction may occur by acceptance or loss of water. Then the liquid of the equilibrium $D . \alpha\, H_2O + D . \beta\, H_2 O + L$ must contain also three components at least. As the solid phases are ternary compounds, the liquid, however, contains already from itself the three components. Consequently we need not add one or more new components, as in the previous system. The composition of the ternary liquid L is completely defined; in general there are two different ternary liquids, which may be in equilibrium with $D . \alpha\, H_2O + D . \beta\, H_2O$.

We now consider the equilibrium;

$$F_1 + F_2 + F_3 \ldots + F_r + L \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (31)$$

The compositions of the solid phases are represented by:

$$\alpha_i Mol\ X + \beta_i Mol\ Y \ldots + (1 - \alpha_i - \beta_i \ldots) Mol\ W$$

$$i = 1, 2 \ldots r$$

that of the liquid L, which contains, besides the components $X\,Y \ldots W$ yet also one or more other components $MN \ldots$ by

$$m\ Mol\ M + n\ Mol\ n \ldots + x\ Mol\ X + y\ Mol\ Y \ldots$$
$$+ (1 - m - n \ldots - x - y \ldots) Mol\ W.$$

We now take in system 31 q quantities of liquid. When the solid substances take δw quantities of the substance W from those q quantities of liquid, then phases-reaction 27 occurs; however, the quantities which participate in this reaction are $\delta w : \mu$ times as large now. The thermodynamical potential of the solid phases changes by this with:

$$-(\lambda_1 \zeta_1 + \lambda_2 \zeta_2 \ldots \lambda_r \zeta_r) \frac{\delta w}{\mu} \quad . \; . \; . \; . \; . \; . \; . \; . \quad (32)$$

that of the total liquid L with

$$\left(-\zeta + m \frac{\partial \zeta}{\partial m} + n \frac{\partial \zeta}{\partial n} \ldots + x \frac{\partial \zeta}{\partial x} + y \frac{\partial \zeta}{\partial y} \ldots\right) \delta w \quad . \; . \; . \quad (33)$$

The total thermodynamical potential of the system 31 changes, therefore, with the sum 32 and 33. As at the equilibrium this change must be zero at constant T and P for each reaction possible in the system, the sum of 32 and 33 is zero, therefore, consequently also their sum when the factor δw is omitted. Hence follows that for 30 we may write also:

$$\delta Z_1 = \left(\zeta - m \frac{\partial \zeta}{\partial m} + n \frac{\partial \zeta}{\partial n} \ldots - x \frac{\partial \zeta}{\partial x} - y \frac{\partial \zeta}{\partial y} \ldots\right) \mu \quad . \; . \quad (34)$$

This means:

the O.W.A. of a system of solid phases between which a phases-reaction may occur by acceptance or loss of the diffusing substance W, is equal to the O.W.A. of each liquid, with which that system of solid phases can be in equilibrium.

Consequently it follows also from this:

all solutions, which can be in equilibrium with a system of solid substances in which a phases-reaction can occur by acceptance or loss of the diffusing substance W, have the same O.W.A. and are isotonic, therefore.

The O.W.A. of the system $Na_2\,SO_4 + Na_2\,SO_4\,.\,10\,H_2O$ is equal, therefore, to that of each arbitrary liquid L of the equilibrium:

$$Na_2SO_4 + Na_2SO_4\,.\,10\,H_2O + L \quad . \; . \; . \; . \; . \; . \quad (35)$$

Above we have seen that this liquid must contain besides the components H_2O and $Na_2\,SO_4$ yet at least one other substance. It is indifferent which are those substances or substance f.i. alcohol, aceton, KCl, sugar etc., provided that only the liquid is in equilibrium with the two solid substances. Consequently an infinite number of liquids exists which may be in equilibrium with $Na_2\,SO_4 + Na_2\,SO_4\,.\,10\,H_2O$; they are all isotonic.

The same is true also for systems as f.i. $Na\,Cl$ + *ice*, $Na_2\,SO_4$ + *ice* etc. and in general for a system; *ice* $+ F_2 + F_3 \ldots$; the phases-reaction which takes place at acceptance or loss of water is then; water $\rightleftarrows$ ice.

The preceding properties are deduced in supposition that the phases of system 26 have a constant composition; however, they are valid also for solid substances with a variable composition (f.i. mixed-crystals) and also when one of the phases is gaseous. Consequently they are true also for a system: water-vapour $+ F_2 + F_3 \ldots$

From the preceding considerations follow at once the results, which we have deduced in the previous communications for simple cases in ternary systems. Let us take f.i. fig. 2 (Communication V); with the aid of the rule, deduced above sub IV. 1. *a*, we find: the O.W.A. of the solid substance X is equal to that of liquid b; that of the hydrate H is equal to that of liquid a and that of the solid mixture $X+Y$ is equal to that of liquid c (and of course equal also to that of the liquids of the isotonic curves, which go through the points b, a and c).

In fig. 3 (Comm. V) the O.W.A. of the ternary compound D is equal to that of liquid s, in fig. 4 it is equal to that of the liquid d. The O.W.A. of the complex $X+D$ is in both figures equal to that of the liquid d and that of $Y+D$ equal to that of liquid c.

A phases-reaction can occur between the phases $Y+H$ in fig. 2 by acceptance and loss of water; with the aid of the rule, deduced sub IV. 3 it follows, that the O. W. A. of $Y+H$ is equal to that of liquid d.

In the equilibria represented by figs. 3 and 4 (Comm. V) also the complex $X+Y+D$ can exist. According to IV. 8 this complex has the same O.W.A. as the liquid in each arbitrary equilibrium:

$$X+Y+D+L \quad \ldots\ldots\ldots \quad (35a)$$

Of course an infinite number of those equilibria exists, but then the liquid must contain, besides the components X Y and W, still one or more other components.

This follows also at once from the figs. 3 and 4; herein viz. no liquid exists, which can be in equilibrium with the three solid substances X Y and D. Yet in the ternary system itself also liquids exist, which have the same O.W.A. as the complex $X+Y+D$. In order to show this we take an arbitrary system:

$$q_1 X + q_2 Y + q_3 D + q L \quad \ldots\ldots\ldots \quad (36)$$

in which q_1 etc. represent the quantities of the different phases. We take q positive and very small with respect to q_1 q_2 and q_3. As, however, this system (36) is not stable, it passes into the complex:

$$q_1' X + q_2' Y + q_3' D \quad \ldots\ldots\ldots \quad (37)$$

We now represent the thermodynamical potentials by ζ_x ζ_y ζ_D and ζ, the composition of

$$D \text{ by } \alpha X + \beta Y + (1-\alpha-\beta)\, W$$
$$L \text{ by } xX + yY + (1-x-y)\, W.$$

With the transition of system (36) into (37) the total thermodynamical potential must decrease; hence follows:

$$\zeta - x\zeta_x - y\zeta_y > (1-x-y)K \quad \ldots\ldots \quad (38)$$

in which

$$K = \frac{\zeta_D - \alpha\zeta_x - \beta\zeta_y}{1-\alpha-\beta} \quad \ldots\ldots\ldots \quad (39)$$

(38) is valid for every arbitrary liquid, therefore, for each value of x and y. If we put $x=0$ and $y=0$ than (38) passes into $\zeta_W > K$, in which ζ_W is the thermodynamical potential of water.

We now imagine a liquid L, which has the same O.W.A. as the complex $X+Y+D$; consequently we have the osmotic equilibrium:

$$\left(X+Y+D \,\middle|\, L\right) \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (40)$$

in which the reaction:

$$aX+\beta y-D+(1-a-\beta)W=0$$

occurs. The composition $x\,y$ of this liquid L of equilibrium (40) is defined by:

$$\zeta-x\frac{\partial\zeta}{\partial x}-y\frac{\partial\zeta}{\partial y}=K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (41)$$

in which K has the value, indicated in (39). Now we may always satisfy (41). For $x=0$ and $y=0$ the first part of (41) becomes ζ_W and, therefore, greater than K. Let we change x and y, then the first part can obtain, therefore, all values between ζ_W and $-\infty$; consequently there are also values of x and y, for which the first part becomes equal to K; consequently we can always satisfy (41). Hence follows, therefore:

in figs. 3 and 4 (Comm. V) is situated anywhere a curve, which represents the solutions, which have the same O.W.A. as the solid complex $X+Y+D$.

We are able to deduce something about the position of this isotonic curve. We imagine in those figs. 3 and 4 each of the three saturation-curves to be drawn totally. That of D then forms a closed curve; $a\,c$ then terminates in a point, which we shall call c', and $b\,d$ in a point which we shall call d'; those points c' and d' are situated on the side XY. As the system $X+Y$ is stable, those curves $a\,c\,c'$ and $b\,d\,d'$ intersect one another in a point s' within the triangle.

We now can show that the point of intersection of the isotonic curve with the saturation-curve $a\,c\,c'\,s'$ is situated on the part $c'\,s'$. For this it is sufficient to show that the solution, which is represented by this point of intersection is supersaturated with respect to the solid substance X.

This solution is defined by the equations:

$$\zeta-x\frac{\partial\zeta}{\partial x}-y\frac{\partial\zeta}{\partial y}=K \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (42)$$

$$\zeta-x\frac{\partial\zeta}{\partial x}+(1-y)\frac{\partial\zeta}{\partial y}=\zeta_y \quad . \quad . \quad . \quad . \quad . \quad . \quad (43)$$

the first of which represents the isotonic curve and the second one the saturation-curve of the solid substance Y. We find from this:

$$\zeta+(1-x)\frac{\partial\zeta}{\partial x}-y\frac{\partial\zeta}{\partial y}-\zeta_x=\frac{\zeta-x\zeta_x-y\zeta_y-(1-x-y)K}{x} \quad . \quad (44)$$

We find this by substituting in the first part of (44) f.i. the values of $\frac{\partial \zeta}{\partial x}$ and $\frac{\partial \zeta}{\partial y}$, which follow from (42) and (43). When the first part should be zero, then this meant that the liquid was in equilibrium with the solid substance X. According to (38) the second part of (44) is positive, however; this means that the liquid is supersaturated with respect to the solid substance X.

Generally we are able to prove now that all liquids of the isotonic curve are supersaturated; consequently this curve is situated totally within the supersaturated region.

The O.W.A. of the solid complex $X + Y + D$ is, therefore, greater than those of the liquids *c* and *d* (figs. 3 and 4 comm. V) and those of all other saturated and unsaturated liquids. When we bring the solid complex in osmotic contact with one of those saturated or unsaturated liquids, then it takes water in and passes into one of the equilibria $X + D +$ liquid *d* or $Y + D +$ liquid *c*.

(To be continued).

Leiden, Lab. of Inorg. Chemistry.

Chemistry. — *"Equilibria in systems in which phases, separated by a semipermeable membrane."* VII. By Prof. F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of March 28, 1925).

Osmotic equilibria and -complexes; the membrane-phase-rule.

We take an osmotic system:

$$E=\left[E_1\,(n_1\,r_1)\mid E_2\,(n_2\,r_2)\right] \quad \ldots\ldots\ldots \quad (1)$$

in which E_1 consists of n_1 components in r_1 phases and E_2 of n_2 components in r_2 phases. Let us take as examples the systems:

$$\left(L\mid L_1\right) \;;\; \left(X+L\mid L_1\right) \;;\; \left(X+Y+L\mid L_1\right) \quad \ldots \quad (2)$$

$$\left(X+X\,.\,n\,H_2O\mid L\right) \quad \ldots\ldots\ldots \quad (3)$$

$$\left(X+Y+X_\alpha\,Y_\beta\,n\,H_2O\mid L\right) \quad \ldots\ldots\ldots \quad (4)$$

in which L and L_1 represent aqueous liquids. If water is the diffusing substance, then a little water may diffuse from right to left and reversally, without a new phase is formed or an existing phase disappears totally. This is always the case when a liquid occurs on both sides of the membrane, as in the systems (2). In the systems (3) and (4) a reaction takes place on the left side on taking in or losing water; this reaction is for system (4):

$$\alpha\,Mol\,X+\beta\,Mol\,Y+n\,Mol\,H_2O \rightleftarrows X_\alpha\,Y_\beta\,.\,n\,H_2O \quad \ldots \quad (5)$$

Let us take now the systems:

$$\left(X\mid L\right) \;;\; \left(X\,.\,n\,H_2O\mid L\right) \quad \ldots\ldots\ldots \quad (6)$$

$$\left(X+Y\mid L\right) \quad \ldots\ldots\ldots \quad (7)$$

$$\left(X+X_\alpha\,Y_\beta\,.\,n\,H_2O\mid L\right) \quad \ldots\ldots\ldots \quad (8)$$

In system (7) and in the first one of the systems (6) no water can diffuse from left to right; if water diffuses from right to left, then on the left side a new phase must arise, f.i. a liquid, a hydrate or water-vapour.

In system (8) and the second one of the systems (6) water is present as well at the right as at the left side of the membrane; with diffusion of water, independent in which direction, a new phase must be formed at the left side.

Consequently, diffusion of a little water causes in the systems (6)—(8) always the occurrence of one or more new phases, so that the system totally changes its character; in the systems (2)—(4), however, only a small change occurs either in the quantities or in the compositions of the phases, which exist already.

For this reason we shall say that the systems (2)—(4) are osmotic equilibria and the systems (6)—(8) complexes. This may be compared f.i. with the systems:

$Na_2SO_4 + Na_2SO_4 \,.\, 10\,H_2O + H_2O$—*vapour*; $Na_2SO_4 + H_2O$—*vapour*;
$Na_2SO_4 \,.\, 10H_2O + H_2O$—*vapour and* $Na_2SO_4 + Na_2SO_4 \,.\, 10\,H_2O$

the first one of which is an equilibrium, but the other three are only complexes, in which nothing may take place without a new phase is formed.

We now take the case that there are two diffusing substances f. i. water and the substance Y. Then the systems (2) and (4) are in osmotic equilibrium with respect to both the diffusing substances. Small quantities of water and Y viz. may diffuse, independent from one another, in both directions, without a new phase is occurring. System (3), however, is only in osmotic equilibrium with respect to water, but not with respect to Y.

The systems (6) are, neither with respect to water, nor with respect to Y, osmotic equilibria, but complexes; system (7) is a complex with respect to water, but an osmotic equilibrium with respect to Y.

System (8) shows something particular; this is viz. a complex, as well with respect to water only as with respect to Y only. If, however, both substances diffuse in a definite ratio viz. n *Mol.* $H_2O : \beta$ *Mol.* Y, then reaction (5) may occur and the complex behaves like an osmotic equilibrium; we will call it preliminarily osmotic.

Consequently we find: with respect to both the diffusing substances the osmotic system can be:

either a complex (system 6)
or an osmotic equilibrium (systems 2 and 4)
or a preliminarily osmotic equilibrium (system 8)
or a complex with respect to the one diffusing substance and an osmotic equilibrium with respect to the other diffusing substance (systems 3 and 7).

If three or more diffusing substances occur, then similar cases may be distinguished.

The membrane-phase-rule.

We take the osmotic equilibrium:

$$E = E_1\,(n_1\,r_1) \,\Big|\, E_2\,(n_2\,r_2) \quad \ldots\ldots\ldots \quad (9)$$

in which E_1 consists of n_1 components in r_1 phases under a pressure P_1 and E_2 of n_2 components in r_2 phases under a pressure P_2. The phase-rule of GIBBS is valid for each of the two systems separately; therefore, at constant temperature E_1 has $n_1 - r_1 + 1$ freedoms and E_2 has $n_2 - r_2 + 1$ freedoms; consequently the total system has $n_1 + n_2 - (r_1 + r_2) + 2$ freedoms.

When E_1 and E_2 are in osmotic equilibrium with one another with respect to the diffusing substance W, then, as we have seen in the previous communication, there is an equation, which expresses that the O.W.A. of E_1 is equal to that of E_2. The total number of freedoms is diminished, therefore, with one.

When E_1 and E_2 are in osmotic equilibrium with respect to d diffusing substances, then there are d equations; the total number of freedoms is diminished, therefore, with d.

Consequently we may say:

the number of freedoms of an osmotic equilibrium:

$$E_1\,(n_1\,r_1) \,\Big|\, E_2\,(n_2\,r_2)$$

in which d diffusing substances occur, is at constant temperature:

$$n_1 + n_2 - (r_1 + r_2) + 2 - d \quad \ldots \ldots \quad (10a)$$

consequently equal to the sum of the freedoms of both systems separately, diminished with the number of diffusing substances.

If we take also the temperature variable, then the number of freedoms becomes:

$$n_1 + n_2 - (r_1 + r_2) + 3 - d \quad \ldots \ldots \quad (10b)$$

We shall apply this to some of the systems, formerly discussed. Let us take f.i. the osmotic equilibrium:

$$E = \left(water \,\Big|\, L \right) \quad \ldots \ldots \quad (11)$$

in which water is the diffusing substance and L a binary liquid. At constant temperature the left system has one freedom and the right one has two freedoms. As there is one diffusing substance, the total system has $1 + 2 - 1 = 2$ freedoms, therefore.

We now give to the water a definite pressure P_0, so that one freedom disappears; consequently the total system has still one freedom. Therefore to each concentration of the liquid L belongs a definite pressure P and consequently also a definite osmotic pressure $P - P_0$ of this liquid.

Let us take the osmotic equilibrium:

$$E = L_1 \,\Big|\, L_2 \quad \ldots \ldots \quad (12)$$

with one diffusing substance f.i. water; we assume that both liquids are ternary. If we keep temperature and pressure constant (the pressure may be for both liquids equal or different) then each liquid has 2 freedoms; the total system has, therefore, $2 + 2 - 1 = 3$ freedoms.

If we take for L_1 a liquid of definite composition, then 2 freedoms disappear; consequently L_2 has still one freedom; it is represented, therefore, in a diagram by a curve. If both liquids have the same pressure and if they consist of the same components, then this is the isotonic curve, formerly discussed, which goes through the point, representing liquid L_1.

We now take some equilibria, which are represented in the figures of the communications III—V. In order to remain in accordance with those diagrams, we assume that there is one diffusing substance viz. $W =$ water and that the pressure of both the separate systems is equal and constant.

In the osmotic equilibrium:

$X + Y + L_1 \mid L$ *figs.* 1 *and* 2. *V* . . . . . (13)

the left system has no more a freedom, as T and P are constant; liquid L_1 must have, therefore, a definite composition viz. c; we represent it by L_c. (13) becomes, therefore:

$X + Y + L_c \mid L$ *figs.* 1 *and* 2. *V* . . . . . (14)

Also in the osmotic equilibria:

$Y + H + L_d \mid L$ *fig.* 2. *V* . . . . (15)

$X + D + L_d \mid L$ *figs.* 3 *and* 4. *V* . . . . (16)

$Y + D + L_c \mid L$ *figs.* 3 *and* 4. *V* . . . . (17)

the liquids on the left side of the membrane must have the indicated composition. As the systems (14)—(17) are osmotic equilibria with one diffusing substance, as the left system is zero and the right one has two freedoms, the total number becomes, therefore, $0 + 2 - 1 = 1$ freedom. Consequently the liquid L is monovariant ($P.T$) and is represented, therefore, by a curve. In system (14) this is the isotonic curve, not-drawn, going through point c, all points of which, except point c itself, represent metastable liquids; in system (15) this is the isotonic curve dn (and its metastable prolongation), etc.

Also the systems:

$Y + H \mid L$ *fig.* 2. *V* . . . . (18)

$X + Y + D \mid L$ *figs.* 3 *and* 4. *V* . . . . (19)

are osmotic equilibria. As in each of those equilibria the system at the left side of the membrane has no freedom, each of those equilibria has, therefore, $0 + 2 - 1 = 1$ freedom. The liquid L is, therefore, monovariant $(P.T)$ again and is represented by the points of a curve. In (18) this is the same as in (15) viz. curve dn; in (19) this is, as we have previously seen, a curve, all points of which represent metastable states.

We now take the osmotic equilibrium:

$$Y + L_1 \mid L \qquad \textit{figs. 1, 2 and 3. III} \quad \ldots \quad (20)$$

in which of course L_1 represents a liquid of wv, viz. of the saturation-curve of Y. As the left system has one freedom and the right one two freedoms, the total equilibrium has, therefore, $1 + 2 - 1 = 2$ freedoms; consequently it is divariant $(P.T)$. If we take for L_1 a definite liquid L_a of the saturation-curve, then one freedom disappears; consequently liquid L has still one freedom. It is represented, therefore, by the points of the isotonic curve an. We shall represent those liquids by $L(1-an)$, in which the 1 indicates that the liquids have one freedom and an is, therefore, a curve. Then we may represent the equilibrium by

$$Y + L_a \mid L(1-an) \qquad \textit{figs. 1, 2 and 3. III} \quad \ldots \quad (21)$$

As we may take for L_1 in (20) each arbitrary liquid of curve wv, we have a.o. also the following equilibria:

$$Y + L_w \mid L(1-wm) \quad ; \quad Y + L_b \mid L(1-bo);\ \textit{etc.} \quad \ldots \quad (22)$$

which represent, therefore, just as (21) special cases of (20).

For the osmotic equilibria

$$H + L_1 \mid L \qquad \textit{fig. 1. IV} \quad \ldots\ldots \quad (23)$$

$$D + L_1 \mid L \qquad \textit{fig. 2. IV} \quad \ldots\ldots \quad (24)$$

the same is valid as for (20). Special cases of (23) are a.o:

$$H + L_w \mid L(1-wm) \quad ; \quad H + L_c \mid L(1-ncn');\ \textit{etc.}$$

and of (24):

$$D + L_w \mid L(1-mwm') \quad ; \quad D + L_f \mid L(1-nfan');\ \textit{etc.}$$

The osmotic system:

$$Y \mid L \qquad \textit{fig. 1. III} \quad \ldots\ldots\ldots \quad (25)$$

is not an equilibrium, but an osmotic complex; as the diffusing substance does not change, therefore, the number of freedoms, this complex has

$0 + 2 = 2$ freedoms. Consequently liquid L is bivariant $(P.T)$ and is represented by the points of a field.

We are able to find the position of this field in the following way. We imagine in (25) the substance Y in equilibrium with a liquid of the saturation-curve wv, f. i. with the liquid a. We then get equilibrium (21). If we take away from this the liquid L_a, then remains the complex:

$$Y \mid L\,(1\text{—}am) \qquad \textit{fig. } 1.\ III \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (26)$$

The solid substance Y can exist, therefore, in osmotic contact with the liquids of curve am; consequently this curve must be situated in the field of the liquid L in (25), which is wanted. If we substitute L_a in (21) by L_w or L_b then we get the equilibria (22); the curves wm and bo are situated, therefore, also in the field wanted.

As we may substitute L_a in (21) by any arbitrary liquid of curve wv, all isotonic curves, going through a point of curve wv, are situated, therefore, in the field. Those curves define a field, which we shall represent by $L\,(2 - wmXv)$; the 2 indicates that the liquids have 2 freedoms and that $wmXv$ is a field, therefore. The wanted field of (25) therefore, must either coincide with the field $wmXv$ or extend itself over it. Further we shall see that it coincides with it. Therefore, the osmotic system (25) is defined more closely by:

$$Y \mid L\,(2\text{—}wmXv) \qquad \textit{fig. } 1.\ III \quad . \quad . \quad . \quad . \quad . \quad (27)$$

Consequently we find, in accordance with our previous considerations:

the solid substance Y may be in osmotic contact with the liquids of the field $wmXv$ without taking water from those liquids. Also we may say, therefore:

the *O. W. A.* of the solid substance Y is smaller than that of the liquids of the field $wmXv$.

In a similar way we find the fields of other osmotic complexes f. i.

$$Y \mid L\,(2\text{—}ambc) \qquad \textit{fig. } 1.\ V \quad . \quad . \quad . \quad . \quad . \quad (28)$$

$$Y \mid L\,(2\text{—}dnbc) \qquad \textit{fig. } 2.\ V \quad . \quad . \quad . \quad . \quad . \quad (29)$$

$$H \mid L\,(2\text{—}wmov) \qquad \textit{fig. } 1.\ IV \quad . \quad . \quad . \quad . \quad (30)$$

$$H \mid L\,(2\text{—}amnd) \qquad \textit{fig. } 2.\ V \quad . \quad . \quad . \quad . \quad . \quad (31)$$

$$D \mid L\,(2\text{—}mwm'p'vp) \quad \textit{fig. } 2.\ IV \quad . \quad . \quad . \quad . \quad (32)$$

Hence appears that the liquids which may be in osmotic contact with the solid substance, without waterdiffusion, are divariant; they are situated in the indicated field.

We are able to deduce those fields also in the following way. We take the osmotic complex:

$$Y \mid L \qquad \text{fig. 1. } III \,.\,.\,.\,.\,.\,.\,.\,.\,. \quad (33)$$

We take in the field, sought for, an arbitrary liquid L_x; as no water diffuses from this towards Y, the O.W.A. of L_x is greater, therefore, than that of the solid substance Y. As L_x changes its place in the field, then it alters its O.W.A., if not, it proceeds along an isotonic curve. We now imagine that L_x changes its place in such a way that its O.W.A. becomes smaller constantly f. i. at a deplacement along a straight line in the direction of point W. At a definite composition of L_x its O.W.A. then becomes equal to that of Y and in (33) a little water may diffuse from L_x towards Y. On the left side of the membrane is then formed a little of the liquid L_w; liquid L_x is represented then by a point of the isotonic curve wm.

If L_x is deplaced still further towards point W, then its O.W.A. becomes smaller perpetually, then the osmotic complex (33) can exist no more. The field sought for is situated, therefore, at the right of curve wm and is, therefore, the field $wmXY$ or, if we limit ourselves to the stable part, the field $wmXv$. We shall represent a similar deduction by:

$$\left.\begin{array}{ll} Y \mid L & \text{fig. 1. } III \\[2ex] Y + L_w \mid L\,(1-wm) & \\[2ex] Y \mid L\,(2-wmXx) & \end{array}\right\} \,.\,.\,.\,.\,.\,.\,. \quad (34)$$

Firstly viz. we write the osmotic complex, the field of which we wish to define, then the osmotic equilibrium which arises with diffusion of a little water and at last the osmotic equilibrium, mentioning the field found.

For the field of the osmotic complex

$$H \mid L \qquad \text{fig. 2. } V \,.\,.\,.\,.\,.\,.\,.\,.\,. \quad (35)$$

we find 2 limit-curves. If a liquid proceeds along a straight line towards the point W, then it gives at a definite composition water to H, so that this passes into $H + L_a$; if this liquid proceeds along the straight line in opposite direction, then its O.W.A. increases and it takes water from H

at a definite composition; this then passes into $Y + H$. We now represent this in a similar way as in (34) viz.

$$\left.\begin{array}{c} H \mid L \qquad \textit{fig. 2. V} \\[1.5em] H + L_a \mid L\,(1-a\,m) \;\Big|\; Y + H \mid L\,(1-d\,n) \\[1.5em] H \mid L\,(2-a\,m\,n\,d) \end{array}\right\} \;\ldots\ldots\ldots \quad (36)$$

The only difference with (34) is that with diffusion of water, now two different osmotic equilibria may occur; at the left side of the line we write the equilibrium, which arises at diffusion of a little water towards the left, at the right side of the line the equilibrium, which arises at diffusion of a little water towards the right. This result is in accordance with that in (31). We now may say:

the hydrate H can be in osmotic contact with the liquids of the field $a\,m\,n\,d$ without it is taking water from those liquids or reversally without it is giving water to them. Liquids, at the left of this field, give water to the hydrate; liquids at the right of this field, take water from the hydrate.

In a similar way we find a.o.:

$$\left.\begin{array}{c} H \mid L \qquad \textit{fig. 1. IV} \\[1.5em] H + L_w \mid L\,(1-w\,m) \;\Big|\; H + L_v \mid L\,(1-v\,o) \\[1.5em] H \mid L\,(2-w\,m\,o\,v) \end{array}\right\} \;\ldots\ldots\ldots \quad (37)$$

which is in accordance with (30)

$$\left.\begin{array}{c} X + Y \mid L \qquad \textit{fig. 1 or 2. V} \\[1.5em] X + Y + L_c \mid L\,(1-c'\,c\,c'') \\[1.5em] X + Y \mid L\,(2-c'\,c\,c''\,X\,Y) \end{array}\right\} \;\ldots\ldots\ldots \quad (38)$$

Herein the isotonic curve (not drawn in the figure) going through point c is represented by $c'\,c\,c''$. The liquids of the field are all supersaturated. As all saturated and unsaturated liquids are situated outside this field, they shall give water to the solid mixture $X + Y$. We may also say, therefore: the O. W. A. of solid $X + Y$ is greater than that of all saturated and unsaturated liquids.

We now take the osmotic complex:

$Y \mid X+L$ *fig.* 1. V . . . . (39)

in which a solid substance is on both sides of the membrane. As the liquid is saturated with solid X, L in (39) can be represented only by points of curve bc. As the *O. W. A.* of the solid substance Y is equal to that of the liquids of curve am, the *O. W. A.* of the solid substance Y is also smaller, therefore, than that of all liquids of curve bc. Consequently we may write for (39):

$Y \mid X+L\,(1-bc)$ *fig.* 1. V . . . . . . (40)

Therefore, the solid substance Y may be in osmotic contact with all liquids, which are saturated with solid X, without taking water from those liquids.

Otherwise it is, however, in the osmotic complex:

$X \mid Y+L$ *fig.* 1. V . . . . (41)

in which the liquids, saturated with Y are represented by points of curve ac. The *O. W. A.* of the substance X is equal to that of the liquids of curve bd; consequently point d divides curve ac into two parts; as the liquids of part dc have a greater O.W.A. than that of liquid d and, therefore, also a greater O.W.A. than the solid substance X, we may write for (41):

$X \mid Y+L\,(1-dc)$ *fig.* 1. V . . . . . . (42)

Consequently the solid substance X cannot be in osmotic contact with all liquids, saturated with solid Y, but only with the liquids, which are represented by part dc of the saturation-curve; if we bring in osmotic contact solid X with liquids of part ad of this saturation-curve, then X shall flow away totally or partially.

(To be continued).

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Chemistry. — *"In-, mono- and plurivariant equilibria"* XXIX. By Prof. F. A. H. SCHREINEMAKERS.

(Communicated at the meeting of March 28, 1925).

Influence of one or more new substances on an equilibrium, in which a phases-reaction may occur.

In the communications XX—XXIII we have discussed already the influence of one new substance on in- and monovariant equilibria; now we shall discuss some more general cases.

We take an equilibrium $E(n.r)(r)$, consequently an equilibrium of n components in r phases, in which a phases-reaction can occur between these r phases. If $r < n+1$, then those phases have to satisfy definite conditions; if $r = n+1$, then this is not necessary. In communication XXVI we have discussed those equilibria $E(n.r)(r)$; they are monovariant and are represented in a PT-diagram by a curve.

By addition of n' new substances to the equilibrium $E(n.r)(r)$ a new equilibrium of $n+n'$ components in r phases arises; as generally no phases-reaction shall occur now between the r phases, the new equilibrium is an equilibrium $E(n+n'.r)$. Only under definite conditions this can form, as we shall see later, an equilibrium $E(n+n'.r)(r)$.

Firstly we shall briefly indicate some examples. If we add to the equilibrium

$$E(1.2) = ice + water \qquad (1)$$

n' new substances XY etc., then arises the equilibrium:

$$E(1+n'.2) = ice + solution\,(XY\ldots) \qquad (2)$$

in which $(XY..)$ indicates that the solution contains, besides the original component (viz. water) yet also the new substances XY etc.

If we add to the equilibrium:

$$E(1.2) = water + vapour \qquad (3)$$

n' new substances, which are all volatile, then arises the equilibrium:

$$E(1+n'.2) = solution\,(XY\ldots) + vapour\,(XY\ldots). \qquad (4)$$

If one or more of the new substances are not volatile, then they disappear in the vapour; if they all are not volatile, then (4) passes into:

$$E(1+n'.2) = solution\,(XY\ldots) + watervapour. \qquad (5)$$

We may add also n' volatile substances to the equilibrium

$$E(1.2) = ice + watervapour$$

so that it passes into

$$E\,(1 + n'.\,2) = ice + vapour\,(XY\ldots) \tag{6}$$

Of course the same is also true if we replace in the previous equilibria the component water by benzene, naphtalene etc.

If we have f.i. the equilibrium:

$$E\,(1\,.\,2) = solid\ \ benzene + liquid\ \ benzene \tag{7}$$

then this can, when the new substances form mixed-crystals with benzene, pass into:

$$E\,(1 + n'.\,2) = mixed\text{-}crystal\,(XY\ldots) + solution\,(XY\ldots). \tag{8}$$

Of course also one or more of the new substances can be missing in the mixed-crystal.

If we add to the equilibria:

$$E\,(2\,.\,3) = solution + Na_2SO_4\,.\,10\,H_2O + Na_2SO_4 \tag{9}$$

$$E\,(2\,.\,3) = watervapour + Na_2SO_4\,.\,10\,H_2O + Na_2SO_4\quad . \tag{10}$$

n' new substances, then they may pass into:

$$E\,(2 + n'.\,3) = solution\,(XY\ldots) + Na_2SO_4\,.\,10\,H_2O + Na_2SO_4\ \ . \tag{11}$$

$$E\,(2 + n'.\,3) = vapour\,(XY\ldots) + Na_2SO_4\,.\,10\,H_2O + Na_2SO_4\quad . \tag{12}$$

With this still also mixed-crystals might be formed with one or both solid phases.

In the equilibria:

$$E\,(n\,.\,2)\,(2) = liquid + vapour \tag{13}$$

$$E\,(n\,.\,2)\,(2) = liquid + mixed\text{-}crystal \tag{14}$$

the two phases have, therefore, the same composition; on addition of n' new substances they pass into:

$$E\,(n + n'.\,2) = liquid\,(XY\ldots) + vapour\,(XY\ldots) \tag{15}$$

$$E\,(n + n'.\,2) = liquid\,(XY\ldots) + mixed\text{-}crystal\,(XY\ldots) \tag{16}$$

In the mixed-crystals and in the vapour one or more or all new substances may miss.

The equilibria $E\,(n\,.\,n+1)$ and $E\,(n\,.\,r)\,(r)$, indicated here, are represented in a PT-diagram by a curve; consequently a definite pressure P_q belongs to a definite temperature T_q and reversally. On addition of the new substances temperature and pressure will be able to change; as we shall see further, we may also keep constant either the temperature or the pressure. Firstly we shall discuss the latter case.

Influence of one or more new substances under constant pressure on an equilibrium, in which a phases-reaction may occur.

If we add to an equilibrium $E\,(n\,.\,r)\,(r)$ under constant pressure P_q the

n' new substances, so that an equilibrium $E(n+n'.r)$ arises, then the temperature will change. Three cases may occur now, viz.

the temperature increases

the temperature decreases

or the temperature increases or decreases or rests unchanged, dependent on the mutual ratio of the new substances.

Although generally without closer examination it is not possible to know, which of those three cases shall occur, yet it is possible in some cases to make a conclusion by a simple discussion.

From the equilibrium $E(n.r)(r)$ may be formed viz. by addition or withdrawal of heat equilibria, in which one or more of the original phases are missing. When we consider the equilibrium $E(n.r)(r)$ under constant pressure at a temperature T_q, then the equilibria which are formed with addition of heat, will be constant at higher temperatures; those which are formed on withdrawal of heat are constant at temperatures lower than T_q.

Consequently we are able to define for each equilibrium $E(n.r)(r)$ which groups of phases exist at temperatures higher than T_q and which groups at temperatures lower than T_q. Let us take f.i. the equilibrium (1); as water arises on addition of heat and ice at withdrawal of heat, the water, therefore, shall exist above 0° and the ice below 0° under a pressure of one atmosphere.

We now add to the equilibrium:

$$E(n.r)(r) = L_0 + M_0 + N_0 \ldots + Q_0 + R_0 \quad . \; . \; . \; . \; (17)$$

the n' new substances, so that it passes into an equilibrium:

$$E(n+n'.r) = L + M + N \ldots + Q + R \quad . \; . \; . \; . \; (18)$$

the phases of which differ little from those of the equilibrium (17). If we add only one of the new substances f.i. X or Y, then we shall represent the new equilibrium by $E(X)$ or $E(Y)$; if we add the three new substances $X\,Y$ and Z, we represent it by $E(X\,Y\,Z)$; etc.

We now add the new substance X only, so that (18) is an equilibrium $E(X)$. In case the new substance does not appear in all phases, we shall divide the phases of (18) into two groups; by $[X]$ we represent the group in which the new substance X occurs; by $[o]$ the group, in which the new substance X does not occur. Consequently we write for (18):

$$E(X) = [o] + [X] \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; (19)$$

This equilibrium can only exist at the temperatures at which the phases-group $[o]$ is constant; as this is known, in accordance with the discussed above, we know also, therefore, the temperatures at which the equilibrium $E(X)$ might exist.

As the same is also true for equilibria $E(Y)$, $E(Z)$, $E(X\,Y)$ etc., it follows:

a. if the new substances are missing in one or more of the phases, then the new equilibrium can exist only at temperatures, at which the phases-group, which is formed by the phases, in which those new substances are missing, is constant.[1]

b. if the new substances occur only in one or more of the phases, which arise at the phases reaction

on addition of heat, then the temperature decreases

on withdrawal of heat, then the temperature increases.

Later we shall deduce this in another way also.

We now shall apply those considerations to some examples. If we add to the equilibrium (1) the n' new substances, so that the equilibrium:

$$E\,(1 + n'.\,2) = ice + solution\,(XY\ldots)$$

arises, then the temperature shall decrease. The new substances do not occur viz. in the ice; according to (*a*) the new equilibrium can exist, therefore, only at temperatures at which the ice exists, consequently (under a pressure of 1 atmosphere) below 0°. This also follows with the aid of (*b*); the new substances viz. occur in the water only, therefore, in the phase, which is formed in (1) on addition of heat; consequently the temperature is lowered.

In the same way it appears that the equilibrium:

$$E\,(1 + n'.\,2) = solution\,(XY\ldots) + water\text{-}vapour$$

which arises by addition of n' substances, which are not volatile, to the equilibrium (3), exists at higher temperatures than equilibrium (3). Consequently the boiling-point of the liquid is raised. We find in this way:

addition of one or more new substances lowers the melting-point and the sublimation-point of solid substances;

addition of new substances, which are not volatile, raises the boiling-point of a liquid.

If the new substances, which we add to equilibrium (3) are volatile, so that an equilibrium:

$$E\,(1 + n'.\,2) = solution\,(XY\ldots) + vapour\,(XY\ldots)$$

arises, then, of course, we cannot apply the rules *a* and *b*. Later we shall see in which way we can find also in this case the change in temperature.

If, however, one of the new substances f. i. X is not volatile, so that an equilibrium:

$$E\,(1 + n'.\,2) = solution\,(XY\ldots) + vapour\,(Y\ldots)$$

arises, then we may conclude anything again. If we omit viz. the volatile substances Y etc. then we get an equilibrium:

$$E\,(X) = solution\,(X) + watervapour,$$

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[1] Compare also communication XXVII of this series.

so that the boiling point of the liquid is raised by addition of the new substance X. However, it rests yet unknown which influence the other substances and their mixtures with X will have on the boiling-point.

Let us take the binary equilibrium:

$$E(2\,.\,3) = F + \textit{solution} + \textit{vapour}$$

in which F is a solid substance. We assume that the phases-reaction:

$$\textit{solution} \rightleftarrows F + \textit{vapour} \quad \ldots\ldots\ldots \quad (20)$$

occurs and that this reaction takes place from left to right on addition of heat. If we add n' substances, which are not volatile, then arises the equilibrium:

$$E(2 + n'\,.\,3) = F + \textit{solution}\,(XY\ldots) + \textit{vapour}$$

so that the known substances do not occur in the phases-group $F +$ vapour; according to reaction (20) this group exists at higher temperatures; according to (*a*) addition of the new substances will cause, therefore, increase of the temperature. The same follows also with the aid of (*b*); the new substances occur viz. only in the solution and this arises, according to (20) on withdrawal of heat.

We may apply those considerations also to equilibria, which consist of one liquid and further of solid substances. The temperature, at which such an equilibrium occurs, may be called the common melting- or inversion-point of those substances. We now assume that heat must be added for the formation of liquid at the phases-reaction; then we find:

the common melting- or inversion-point of a mixture of solid substances is lowered by the addition of new substances, if those occur in the liquid only.

We add to the equilibria (13) and (14) new substances, which occur in the liquid only; we then get the equilibria:

$$E(n + n'\,.\,2) = \textit{liquid}\,(XY\ldots) + \textit{vapour} \qquad (21)$$

$$E(n + n'\,.\,2) = \textit{liquid}\,(XY\ldots) + \textit{mixed-crystal} \qquad (22)$$

Let us call the composition of the vapour in equilibrium (13) G_0 and that of the mixed-crystals in (14) M_0. The vapour, which is formed, on increase of T from equilibrium (13) shall, therefore, have also the composition G_0; and the mixed-crystal, which is formed on decrease of T from equilibrium (14) will have the composition M_0.

In the equilibria (21) and (22) vapour and mixed-crystal may have, however, an infinite number of compositions, which differ from G_0 and M_0. Consequently it is not allowed to apply the former rules without more, to all the equilibria (21) and (22); it is allowed, however, if we choose from the infinite number of equilibria, those, in which the vapour has the composition G_0 and the mixed-crystal the composition M_0. Consequently we may conclude that of all equilibria (21) surely one exists at higher temperatures and of all equilibria (22) surely one at lower temperatures. An examination more in detail may, as we shall see further, decide with regard to the other equilibria.

In order to elucidate the previous general considerations further, we represent the phases-reaction, which may take place in the equilibrium:

$$E\,(n\,.\,r)\,(r) = L_0 + M_0 + N_0 \ldots + Q_0 + R_0 \quad \ldots \quad (23)$$

between the r phases by:

$$\varrho_1 L_0 + \varrho_2 M_0 + \varrho_3 N_0 \ldots + \varrho_r R_0 = 0 \quad \ldots \quad (24)$$

so that $\Sigma(\varrho) = \varrho_1 + \varrho_2 \ldots + \varrho_r = 0$. Consequently we are able to express one of the phases f.i. L_0 in the $r-1$ other ones viz.

$$L_0 = a_1 M_0 + a_2 N_0 + \ldots + a_{r-1} R_0 \quad \ldots \quad (25)$$

in which $\Sigma\,(a) = a_1 + a_2 \ldots a_{r-1} = 1$. From (24) and (25) follow the relations:

$$\varrho_1 a_1 + \varrho_2 = 0 \qquad \varrho_1 a_2 + \varrho_3 = 0 \ldots \varrho_1 a_{r-1} + \varrho_r = 0 \quad \ldots \quad (26)$$

in which $\Sigma\,(\varrho) = 0$ is included.

In order to represent an equilibrium, the phases of which differ a little from those of the equilibrium (23), we have to take n composants; for this we take the $r-1$ phases $M_0 \ldots R_0$ and further still $n-r+1$ arbitrary phases $U\,V$ etc. In order to represent the equilibrium:

$$E\,(n + n'.\,r) = L + M + N \ldots + Q + R \quad \ldots \quad (27)$$

we need still n' new composants; for this we take the n' new substances XY etc. We now can represent an arbitrary phase F of the equilibrium (27) by:

$$F = xX + yY \ldots + uU \ldots + mM_0 + nN_0 \ldots + qQ_0 + rR_0 \quad . \quad (28)$$

in which we take $r = 1 - x \ldots - q$. In order to represent the r phases of the equilibrium (27) we give in (28) to the variables successively the indices $1, 2 \ldots r$.

If we put further:

$$\zeta - x\frac{\partial \zeta}{\partial x} - y\frac{\partial \zeta}{\partial y} \ldots - u\frac{\partial \zeta}{\partial u} \ldots - m\frac{\partial \zeta}{\partial m} - n\frac{\partial \zeta}{\partial n} \ldots - q\frac{\partial \zeta}{\partial q} = \varphi \,. \quad (29)$$

then for the equilibrium (27) the $r-1$ equations:

$$\varphi_1 = \varphi_2 = \ldots = \varphi_{r-1} = \varphi_r \quad \ldots \quad (30)$$

are true.

We find $\varphi_1\,\varphi_2$ etc. by giving in (29) to all letters successively the indices $1, 2 \ldots r$.

Further we still have the equations:

$$\left(\frac{\partial \zeta}{\partial x}\right)_1 = \left(\frac{\partial \zeta}{\partial x}\right)_2 = \ldots = \left(\frac{\partial \zeta}{\partial x}\right) \quad \ldots \quad (31)$$

and those, which follow herefrom, if we replace x successively by the other variables of (28). Consequently in (31) we find $n + n' - 1$ series, each of $r-1$ equations; therefore, together $(n+n'-1)(r-1)$ equations. Consequently we have in total $(n+n')(r-1)$ equations; if we keep the pressure constant, then there are $(n+n'-1)r+1$ equations; therefore, equilibrium (27) has $n+n'-r+1$ equations. If $r=n+1$, as in the examples 1—12, then the number of freedoms becomes n', consequently equal to the number of new substances, which are added.

If the equilibrium $E(n\,.\,r)(r)$ exists at the temperature T_q then we consider the equilibrium $E(n+n'\,.\,r)$ at the temperature $T_q + \triangle T$; further we assume that the phases of both equilibria differ only very little from one another.

In (29) and (31) $\frac{\partial \zeta}{\partial x}, \frac{\partial \zeta}{\partial y}$ etc. which refer to the new components, get infinitely large; for this we put:

$$\zeta = \zeta' + RT(x \log x + y \log y + \ldots) \quad . \quad . \quad . \quad . \quad . \quad (32)$$

in which we take between parentheses only the variables of the n' new substances. From this follow a. o. the equations:

$$\left.\begin{array}{c} \frac{\partial \zeta}{\partial x} = \frac{\partial \zeta'}{\partial x} + RT(1+\log x) \qquad \frac{\partial \zeta}{\partial y} = \frac{\partial \zeta'}{\partial y} + RT(1+\log y) \\ -\eta = \frac{\partial \zeta'}{\partial T} + R(x \log x + y \log y + \ldots) \end{array}\right\} \quad . \quad (33)$$

With the aid of those equations the n' first series of the equations (31) pass into:

$$\left.\begin{array}{l} \frac{x_1}{\alpha_1} = \frac{x_2}{\alpha_2} = \ldots = \frac{x_r}{\alpha_r} \\ \frac{y_1}{\beta_1} = \frac{y_2}{\beta_2} = \ldots = \frac{y_r}{\beta_r} \end{array}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (34)$$

etc. For infinitely small values of those variables the denominators (viz. the $r-1$ ratio's in each series) approach to definite values.

Hence follows:

the division of the new substances XY etc. over the r phases of the equilibrium $E(n+n'\,.\,r)$ is not arbitrary. The division of substance X is defined by the first series of the equations (34); that of substance Y by the second series etc.

If, therefore, we know the quantity of one of the new substances f.i. of X in one of the r phases, then, in accordance with (34) we know also the quantity of this substance X in each of the other $r-1$ phases.

The $n-1$ other series of (31) become:

$$\triangle\left(\frac{\partial \zeta}{\partial u}\right)_1 = \triangle\left(\frac{\partial \zeta}{\partial u}\right)_2 = \ldots = \triangle\left(\frac{\partial \zeta}{\partial u}\right)_r \quad . \quad . \quad . \quad . \quad . \quad (35)$$

and still $n-2$ other series. The sign $\triangle$ indicates with this that we have to differentiate with respect to all variables, also T.

From (30) follow the equations:

$$\triangle \varphi_1 = \triangle \varphi_2 = \ldots = \triangle \varphi_r \quad . \; . \; . \; . \; . \; . \; . \quad (36)$$

In order to find them we substitute in (29) the necessary values from (32) and (33); then we find:

$$\zeta' - RT(x+y+\ldots) - x\frac{\partial \zeta'}{\partial x} \ldots - u\frac{\partial \zeta'}{\partial u} \ldots - m\frac{\partial \zeta'}{\partial m} \ldots - q\frac{\partial \zeta'}{\partial q} = \varphi \quad . \quad (37)$$

Between the parantheses are placed only the variables, which refer to the new substances.

In order to find the values of $\triangle \varphi_1$ etc., we have to bear in mind the following. If F in (28) has to present the phase L of (27), which must differ infinitely little from L_0, then we have to put, according to (25):

$$m_1 = a_1 + \triangle m_1 \quad n_1 = a_2 + \triangle n_1 \ldots . \; q_1 = a_{r-1} + \triangle q_1$$

while $x_1\, y_1 \ldots u_1 \ldots$ are infinitely small.

In order to represent phase M of (27) we put $m_2 = 1 + \triangle m_2$, while we take all other variables $x_2 \ldots . q_2$ infinitely small.

If we do in similar way for the other phases, then we find:

$$\left.\begin{aligned} \triangle \varphi_1 = & - \eta_1 \triangle T - RT_q (x_1 + y_1 \ldots) \\ & - a_1 \triangle \frac{\partial \zeta'}{\partial m} - a_2 \triangle \frac{\partial \zeta'}{\partial n} \ldots - a_{r-1} \triangle \frac{\partial \zeta'}{\partial q} - R_1 \end{aligned}\right\} \quad . \quad (38)$$

$$\left.\begin{aligned} \triangle \varphi_2 \; & = - \eta_2 \; \triangle T - RT_q (x_2 \; + y_2 \; \ldots) - \triangle \frac{\partial \zeta'}{\partial m} - R_2 \\ & . \; . \\ \triangle \varphi_{r-1} & = - \eta_{r-1} \triangle T - RT_q (x_{r-1} + y_{r-1} \ldots) - \triangle \frac{\partial \zeta'}{\partial q} - R_{r-1} \\ \triangle \varphi_r \; & = - \eta_r \; \triangle T - RT_q (x_r \; + y_r \; \ldots) - R_r \end{aligned}\right\} \quad . \quad (39)$$

According to (35) we may give in this each arbitrary index from 1 up to r to $\triangle \frac{\partial \zeta'}{\partial m}$; $\eta_1\, \eta_2$ etc. are the entropies of the phases $L_0\, M_0$ etc.; $R_1\, R_2$ etc. contain the terms, which are of higher order.

We shall replace (38) by another equation: for this we add the equations (38) and (39) after having multiplied them successively with $\varrho_1\; \varrho_2 \ldots \varrho_r$. We then get, with the aid of (26) and (36):

$$o = + \Sigma (\varrho \eta) . \triangle T + RT_q \; \Sigma \varrho (x + y \ldots) + \Sigma (\varrho R) \quad . \quad . \quad (40)$$

Herein is $\Sigma (\varrho \eta) = \varrho_1 \eta_1 + \varrho_2 \eta_2 \ldots + \varrho_r \eta_r$ the change in entropy, when in the equilibrium $E(n \, . \, r)(r)$ the phases-reaction (24) occurs. We will choose the direction of this reaction always in such a way that heat must be added; then $\Sigma (\varrho \eta)$ is positive.

Further we have:

$$\Sigma \varrho (x + y \ldots) = \varrho_1 (x_1 + y_1 \ldots) + \varrho_2 (x_2 + y_2 \ldots) \ldots + \varrho_r (x_r + y_r \ldots)$$

so that we may write also:

$$\Sigma\, \varrho\, (x + y \ldots) = \Sigma\, (\varrho\, x) + \Sigma\, (\varrho\, y) + \ldots$$

Each of those terms $\Sigma\ (\varrho x)$, $\Sigma\ (\varrho y)$, etc. contains, on account of the equations (34), only one independent variable.

Firstly we put $r = n + 1$ so that the equilibrium has n' freedoms. We now are able to satisfy the equations by taking all variables of the same order; (40) then passes into:

$$(\triangle T)_P = -\frac{RT_q}{\Sigma\ (\varrho\, \eta)} \cdot \Sigma\, \varrho\, (x + y \ldots) \quad \ldots\ldots \quad (41)$$

or

$$(\triangle T)_P = -\frac{RT_q}{\Sigma\ (\varrho\, \eta)} [\Sigma\ (\varrho\, x) + \Sigma\ (\varrho\, y) \ldots] \quad \ldots \quad (42)$$

in which $(\triangle T)_P$ indicates that the change in T takes place under constant pressure. This change in T depends, therefore, only on the quantities of the new substances $X\ Y$ etc. in the different phases.

We now let the phases-reaction (24) take place in such direction that the entropy increases; then $\Sigma\ (\varrho\, \eta)$ is positive. The phases, which are formed with this reaction, then have a positive coëfficient in (24); the phases which disappear with this reaction, have a negative coëfficient in (24). Those coëfficients and the quantities $x_1\, x_2 \ldots y_1\, y_2$ etc. define the value of $\Sigma\, \varrho\, (x + y \ldots)$; if this form is positive, then the temperature decreases; if it is negative, the temperature increases. In some cases this sign is known without further examination. If the new substances occur f. i. only in one or more of the phases, which arise on addition of heat, then, therefore, in $\Sigma\, \varrho\, (x + y \ldots)$ only positive terms remain; in accordance with (41) the temperature is lowered, therefore. If the new substances occur only in one of more of the phases, which arise on withdrawal of heat, then in $\Sigma\, \varrho\, (x + y \ldots)$ only negative terms remain, consequently the temperature is raised.

Therefore, we refind here the rule, mentioned above sub *b*.

We may still write otherwise (42); with the aid of (34) we are able to express n of the $n + 1$ variables $x_1\, x_2$ etc. in one of them; also n of the $n + 1$ variables $y_1\, y_2$ in one of those, etc. Instead of (42) we can write, therefore:

$$(\triangle T)_P = -\frac{RT_q}{\Sigma\ (\varrho\, \eta)} (\alpha x + \beta y \ldots) \quad \ldots\ldots \quad (43)$$

in which we may give to $x\, y$ etc. each index from 1 till $n + 1$; $\alpha\, \beta$ etc. have definite positive or negative values, which, however, are dependent on the indices, which we give to $x\, y$ etc.

If we add the new substance X only, then (43) passes into:

$$(\triangle T)_P \,.\, (X) = -\frac{RT_q}{\Sigma\ (\varrho\, \eta)} \cdot \alpha\, x \quad \ldots\ldots \quad (44)$$

In order to indicate that the change in temperature is a result only of the addition of the substance X, still (X) is placed behind $(\triangle T)_p$. It is apparent from (44) that the sign of α decides whether the temperature must be raised or lowered.

It is evident now that we may write for (43) also:

$$(\triangle T)_P = (\triangle T)_P(X) + (\triangle T)_P(Y) + \ldots \quad \ldots \quad (45)$$

This means that the total change in temperature is the algebraic sum of the changes in T, which each of the new substances would cause, if they were added separately.

Consequently, if each new substance gives by itself an increase (decrease) of T, then their mixture gives also an increase (decrease) of T.

If, however, some of the added substances, give an increase of T and other ones an decrease of T, then it depends on their mutual ratio, whether their mixture will raise or lower the temperature.

Therefore it must be possible, to add the new substances in such ratio that no change in temperature occurs.

Then must be satisfied:

$$\alpha x + \beta y + \ldots = 0 \quad \ldots \ldots \ldots \quad (46)$$

in which, as $x\,y$ etc. are always positive, not all coefficients are able to have the same sign. In general (46) can be satisfied by an infinite number of ways; consequently there is an infinite number of mixtures, which let the temperature unchanged. Of course this is only true at first approximation, for it follows from (40) that $\triangle T$ is a quantity of the second order.

(To be continued).

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Mathematics. — *"On Polar Triangles"*. By Prof. W. VAN DER WOUDE. (Communicated by Prof. J. C. KLUYVER).

(Communicated at the meeting of February 28, 1925).

Dr. G. SCHAAKE has given and investigated a representation of the polar triangles of a conic on the points of a three-dimensional space [1]. My aim is only to represent the same elements on each other. The result is the same as that of Dr. SCHAAKE. As, however, the method followed by me is very different from that of my predecessor, it seemed allowed to treat the same subject once more.

Besides the conic $\bar{a}$ a complex of conics C is assumed relative to which $\bar{a}$ lies "arbitrarily". Each of these conics has a polar triangle in common with $\bar{a}$ and generally only one. We can, therefore, consider the 4 homogeneous parameters $(\varkappa, \lambda, \mu, \nu)$ through which a conic $\bar{c}$ of C is defined, at the same time as coordinates of that common polar triangle. If then we consider $(\varkappa, \lambda, \mu, \nu)$ as homogeneous coordinates in space, the conics of C as well as the polar triangles of $\bar{a}$ are represented on the points of space.

§ 1. Let $\bar{a}$ be given by the equation:

$$\bar{a} \equiv a_{11}\, x_1^2 + a_{22}\, x_2^2 + a_{33}\, x_3^2 + 2a_{23}\, x_2\, x_3 + 2a_{13}\, x_1\, x_3 + 2a_{12}\, x_1\, x_2 = 0 \quad . \; (1)$$

The equation of the complex C gets the most simple form if we give the four double lines that are contained in the complex, the equations:

$$x_1 = 0, \quad x_2 = 0, \quad x_3 = 0, \quad x_1 + x_2 + x_3 = 0.$$

In this case C is represented by:

$$C \equiv \varkappa x_1^2 + \lambda x_2^2 + \mu x_3^2 + \nu\,(x_1 + x_2 + x_3)^2 = 0 \quad . \quad . \quad . \quad . \quad (2)$$

If we consider at the same time $(\varkappa, \lambda, \mu, \nu)$ as homogeneous coordinates in space, each set of them, as remarked before, represents a conic $\bar{c}$ of C as well as the polar triangle (or triangles) common to $\bar{a}$ and $\bar{c}$ on the points of three-dimensional space.

§ 2. In order to find the singular elements of the representation it is necessary to investigate:

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[1] Dr. G. SCHAAKE: Representation of the Polar Triangles of a Conic Section on the Points of Space. These Proceedings, **27**, p. 584.

1. the conics $\bar{c}$ that have more than one polar triangle in common with $\bar{a}$.

2. the polar triangles of $\bar{a}$ that are common to $\bar{a}$ and more than one conic $\bar{c}$.

Both problems are intimately related with that on the double lines of the quadruply infinite linear system of conics Σ defined by C and $\bar{a}$. For this reason we begin by investigating the locus of these double lines.

The system Σ is defined by:

$$\left.\begin{array}{l}\Sigma \equiv C + \varrho\bar{a} \equiv \varkappa x_1^2 + \lambda x_2^2 + \mu x_3^2 + \nu\,(x_1 + x_2 + x_3)^2 + \\ + \varrho\,(a_{11}\,x_1^2 + a_{22}\,x_2^2 + a_{33}\,x_3^2 + 2a_{23}\,x_2\,x_3 + 2a_{13}\,x_1\,x_3 + 2a_{12}\,x_1\,x_2) = 0\end{array}\right\} \quad . \; . \; (3)$$

If a double line

$$(\xi_1\,x_1 + \xi_2\,x_2 + \xi_3\,x_3)^2 = 0$$

belongs to Σ, it must be possible to determine $\varkappa, \lambda, \mu, \nu, \varrho$ and σ so that

$$\left.\begin{array}{l}\sigma\xi_1^2 = \varkappa + \nu + \varrho a_{11} \\ \sigma\xi_2^2 = \lambda + \nu + \varrho a_{22} \\ \sigma\xi_3^2 = \mu + \nu + \varrho a_{33}\end{array}\right\} \qquad \left.\begin{array}{l}\sigma\xi_2\,\xi_3 = \nu + \varrho a_{23} \\ \sigma\xi_1\,\xi_3 = \nu + \varrho a_{13} \\ \sigma\xi_1\,\xi_3 = \nu + \varrho a_{12}\end{array}\right\} \quad . \; . \; . \; (4)$$

For this it is necessary and sufficient that between ξ_1, ξ_2, ξ_3 there exists the relation

$$\Delta \equiv \begin{vmatrix} 1 & a_{23} & \xi_2\xi_3 \\ 1 & a_{13} & \xi_1\xi_3 \\ 1 & a_{12} & \xi_1\xi_2 \end{vmatrix} = 0 \quad . \; . \; . \; . \; . \; . \; (5)$$

As appears from the fact of a simultaneous invariant becoming zero, this is the tangential equation of the conic harmonically inscribed in all the conics of Σ; the poles of their tangents form a conic δ, the reciprocal polar curve of Δ relative to $\bar{a}$. In other terms:

The double lines of Σ envelop a conic Δ; we may arrange them in an involution of the third order of which each triple forms the sides of a polar triangle of $\bar{a}$.

§ 3. If a conic $\bar{c}$ is to have more than one polar triangle in common with $\bar{a}$, it must touch $\bar{a}$ twice and, therefore, define with $\bar{a}$ a pencil which contains a double line; this double line belongs to Σ. Inversely: each double line of Σ defines a conic $\bar{c}$ of C which touches $\bar{a}$ twice.

We try to find the relations that must exist between $\varkappa, \lambda, \mu, \nu, \varrho$ if this double contact is to take place. They are found by eliminating ξ_1, ξ_2, ξ_3 out of (4) and they are:

$$\left.\begin{aligned}(\varkappa + \nu + \varrho a_{11})(\nu + \varrho a_{23}) - (\nu + \varrho a_{12})(\nu + \varrho a_{13}) = 0\\ (\lambda + \nu + \varrho a_{22})(\nu + \varrho a_{13}) - (\nu + \varrho a_{12})(\nu + \varrho a_{23}) = 0\\ (\mu + \nu + \varrho a_{33})(\nu + \varrho a_{12}) - (\nu + \varrho a_{13})(\nu + \varrho a_{23}) = 0\end{aligned}\right\} \quad . \quad . \quad . \quad (6)$$

In this way $\frac{\varkappa}{\varrho}, \frac{\lambda}{\varrho}, \frac{\mu}{\varrho}$ are expressed rationally in $\frac{\nu}{\varrho}$; if we put

$$\frac{\nu}{\varrho} = t,$$

we have e.g.

$$\frac{\varkappa}{\varrho} = -(a_{11} + t) + \frac{(a_{12} + t)(a_{13} + t)}{a_{23} + t}.$$

If we consider $\varkappa, \lambda, \mu, \nu$ as homogeneous coordinates in space, (6) represents a rational twisted curve of the fourth order.

The singular points in space form a rational twisted curve r^4 *of the fourth order circumscribed about the coordinate-tetrahedron of which each point corresponds to a conic* $\bar{c}$ *touching* a *twice and also to an infinite number of polar triangles that are common to* $\bar{a}$ *and* $\bar{c}$*. The common side of these triangles touches* $\triangle$*; the common angular point lies on* δ*. Only one of these triangles is circumscribed about* $\triangle$ *and inscribed in* δ*; each of the sides of this triangle is a double line of* Σ (§ 2).

§ 4. If a polar triangle is common to $\bar{a}$ and more than one conic, hence at least to a pencil of C, Σ must belong to a net which contains $\bar{a}$, and which has this triangle as polar triangle. Accordingly the three sides are double lines of Σ; they form one of the involutorial triangles that are circumscribed about $\triangle$ and are polar triangles of $\bar{a}$. Inversely we found already that each double line of Σ defines only one involutorial triangle.

Consequently to each involutorial triangle there corresponds a net of Σ, hence a pencil of C, of which it is the common polar triangle; to each involutorial triangle there corresponds, therefore, a pencil of conics, hence a straight line in three-dimensional space.

Three conics $\bar{c}$, however, belong to this pencil each of which touches $\bar{a}$ in the two points of intersection with the sides of the involutorial triangle and corresponds accordingly to a point of r^4. Hence we have found:

The singular elements of the plane consist of the involutorial triangles, i.e. the polar triangles of a *that are circumscribed about* $\triangle$ *and inscribed in* δ*. To each of these triangles there corresponds a pencil of conics and in space a trisecant of* r^4*.*

In this way we have found the singular elements; a further discussion of the representation was not our aim. For this we refer to the detailed paper of Dr. SCHAAKE.

Astronomy. — *"The proper motion of the globular cluster Messier 13 and its internal motion."* By ADRIAAN VAN MAANEN.

(Communicated at the meeting of January 31, 1925).

The unexpected discovery of internal motions in the spiral nebulae, from the study of photographs with a relatively short interval made it seem desirable to try analogous measures for one or more globular clusters.

Several photographs of globular clusters were obtained soon after the 80-foot focus arrangement of the 60-inch Mount Wilson reflector had been made available for direct photography (1913). After an interval of over ten years I have measured some plates of the great cluster in Hercules Messier 13, two pair of plates of good quality and with an interval of 9 and 11 years, respectively, being chosen for measurement, which was done with the stereocomparator, with the plates in four positions, East, West, North, and South, respectively, in the direction of the increasing readings of the micrometer screw.

Dr. SHAPLEY had indicated which stars might be members of the cluster and which not, the latter to be used for comparison purposes. With his help fifty comparison stars were selected while sixty-two other stars were measured, which, with considerable probability, might be accepted as members of the cluster. His selection was based on the distance from the center, the magnitude, and the color-index of the individual stars.

As the detailed measures will be published in *Contributions of the Mount Wilson Observatory* N⁰. 284, I shall here give only the results.

That the motions of the members of the cluster are small was at once evidenced by the fact that the annual motions, regardless of the algebraic sign, are only 0''.003 in both right ascension and declination, while the analogous values for the comparison stars are 0''.006 and 0''.010 respectively.

Taking account of the algebraic sign of the motions, we derive for the motion of the cluster with respect to the mean motion of the comparison stars:

$$\mu_\alpha = -0''.001 \pm 0''.0004$$
$$\mu_\delta = -0''.001 \pm 0''.0003.$$

Subtracting these quantities from μ_α and μ_δ of the individual members of the group, we derive values which represent the internal motions in the cluster. As we might *a priori* expect a contraction or a dispersion, the first thing to do was to derive the mean radial component of the motion. The result is, however, that this component is 0''.0000 ± 0''.0003;

there is little reason to anticipate a component at right angles to the radius, except that in the measures of the spiral nebulae such a component has been shown to exist. In Messier 13 this component is 0″.0005 ± 0″.0004 in the direction N W S E. We may thus conclude that the internal motions in the cluster are of the order of 0″.001 or less.

Similar result can be derived in the following way: the probable error of the motion in each coordinate as derived from a comparison of the measures of each pair of plates is 0″.0023. If we accept all the 62 stars as real members of the group and that therefore, except for any possible internal motions, they all must have the same motion, we can derive a probable error from the deviations from this mean motion of the group; the result is 0″.0026. It is true that this is slightly larger than the value 0″.0023 found before, but it is a well known fact that the internal probable error is always somewhat, and sometimes considerably smaller than the external probable error. The difference between the two values given indicates that the internal motions of the members of the group can scarcely exceed 0″.001 in each coordinate.

The results of the measures are thus negative: the motions are too small to be detected in an interval of ten years; they are, nevertheless, of importance for two reasons: firstly, they show that the parallax of 0″.00009, derived by Shapley for Messier 13, cannot be very much too small, as otherwise with the considerable radial velocities found for the globular clusters, we might have expected a measurable motion at right angles to the line of sight; and secondly, the results are of importance in connection with the internal motions found in several spiral nebulae. The plates were taken and measured with the same instruments as in the case of the nebulae and the possibility that their internal motions, which were found to be of the order of 0″.020 annually, are due either to the 60-inch reflector or to the stereocomparator, is therefore eliminated. The only possibility that the displacements found in the spirals are not real motions would seem to lie in a systematic difference along the arms of the spirals between the old and the new plates. This possibility is extremely doubtful, because in that case the total displacements would hardly be proportional to the time interval, as was found in several of the spirals for which pairs of plates with different time intervals were available. Moreover, such displacements should be quite different in spirals with a large amount of nebulosity present and in objects where the nebula is practically resolved into individual starlike points. Finally, if the displacements were due to some photographic effect, we should expect such a systematic error to be larger near the centre than near the edge of the spiral, while the measures show just the reverse in all cases.

Mathematics. — "*Representation of the Pairs of Points Conjugated relative to a Conic, on the Points of Space.*" By G. SCHAAKE. (Communicated by Prof. JAN DE VRIES.)

(Communicated at the meeting of January 31, 1925.)

§ 1. Let a conic k^2 in a plane α be the projection on α of a twisted cubic k^3 out of a point A of the latter cubic. If we associate to each point P of k^3 its projection Q on α, there arises a one-one correspondence (P, Q) between the points P of k^3 and the points Q of k^2 where the point of intersection B on k^2 of the tangent a at A to k^3 with α corresponds to the point A of k^3.

Let C_1 and C_2 be two points of a associated to each other relative to k^2. The lines BC_1 and BC_2 cut k^2 outside B resp. in K_1 and K_2. The tangents t_1 and t_2 which may be drawn to k^2 resp. at K_1 and K_2, have their point of intersection C on the line l joining C_1 and C_2. For the pairs (K_1, K_2) which may be derived from the pairs (C_1, C_2) of the involution defined on l by k^2, form an involution on k^2 the double points of which lie in the points of intersection Q_1 and Q_2 of l with k^2 and which, therefore, has l as axis.

The plane (A, l) contains one chord k of k^3 which does not pass through A, the line joining the points P_1 and P_2 of the twisted cubic that correspond to Q_1 and Q_2. We consider the point of intersection S of the lines AC and k as the image of the pair of points (C_1, C_2).

Inversely a pair of points C_1 and C_2 that are associated relative to k^2, may be derived from any point S. With a view to this we draw the chord k of k^3 through S. We project k and S on α out of A and find the line l and the point C on l. We determine the points of contact K_1 and K_2 of the tangents t_1 and t_2 to k^2 through C. C_1 and C_2 are resp. the points of intersection of BK_1 and BK_2 with l.

In this way we have found a representation of the pairs of points C_1 and C_2 associated to each other relative to k^2, on the points S of space.

§ 2. In order to arrive at another way to produce our representation, we examine what corresponds to the system S_1 of the ∞^1 pairs of points associated relative to k^2, for which C_1 is a fixed point of α. In this case K_1, the point of intersection of BC_1 and k^2, is the same point of this conic for all the individuals of S_1 and t_1 is a fixed tangent of k^2. The point S always lies in the tangent plane τ_1 through t_1 to the cone $\varkappa$ which projects k^3 out of A. The chords k which contain the image points S of the pairs of points of S_1, from the scroll ϱ of the chords of k^3 which cut the straight line AC_1, as the projections of these chords on α, i.e. the lines l of S_1, all pass through C_1. The generatrix of ϱ through A lies in the plane ABC_1 through AC_1 and the tangent a, joins A to the point of intersection of that plane and k^3, and is accordingly the line AK_1 in τ_1.

The locus of the points of intersection of the lines of ϱ with τ_1 is consequently a line s_1 of the scroll σ associated to ϱ, which passes through the point of intersection L_1 outside A of AK_1 with k^3, as the quadratic surface φ^2 that contains ϱ and σ, touches the plane τ_1 at L_1. For the tangent plane to φ^2 at L_1 is completely defined by the tangent to k^3 and AK_1.

The system of the ∞^1 *pairs of points conjugated relative to* k^2 *of which one point is given, is accordingly represented on a line* s_1 *which touches the cone* $\varkappa$ *on* k^3.

§ 3. The straight line s_1 corresponding to a given point C_1 of α according to § 2, may be found in the following way. We consider the scroll ϱ of the chords of k^3 which cut the line AC_1. The generatrices of the corresponding scroll σ which meet k^3 once, all cut the generatrix AK_1 of ϱ through A which passes through the point of intersection K_1 outside B of BC_1 with k^2, and are, therefore, projected on α as straight lines through K_1. Among the lines through K_2 there is one, t_1, which touches k^2, so that σ contains one line s_1 which touches $\varkappa$ on k^3, and that in the point of intersection L_1 outside A of AK_1 and k^3. This line is the line s_1 corresponding to C_1.

The point C_1 of α which corresponds to a line s_1 which touches $\varkappa$ on k^3, is found in the following way. We form the scroll ϱ of the chords k of k^3 which cut s_1. The generatrice through A of the scroll σ associated to ϱ, cuts α in C_1.

The lines s which are represented in this way on the points of α, form a congruence Σ (2, 3). For the lines s through a point S of space have their points of contact in the two points of intersection outside A of the polar plane of S relative to $\varkappa$ with k^3, and the lines s lying in a given plane φ are the tangents that may be drawn in the points of intersection of φ with k^3 to the conic along which φ cuts the cone $\varkappa$.

Consequently the pair of points (C_1, C_2) *corresponding in the representation of § 1 to a given point* S *of space, is formed by the two points* C_1 *and* C_2 *that are associated to the lines* s_1 *and* s_2 *through* S *of* Σ. *Inversely the image* S *of a pair of points* (C_1, C_2) *associated relative to* k^2, *is the point of intersection of the lines* s_1 *and* s_2 *corresponding to* C_1 *and* C_2.

§ 4. If we choose S on the cone $\varkappa$, s_1 and s_2 coincide in the generatrix AS of $\varkappa$ through S which cuts k^3 besides in A in L, where L_1 and L_2, the points in which s_1 and s_2 touch the cone $\varkappa$ on k^3, coincide.

The scroll ϱ and the associated scroll σ are both formed by the generatrices of $\varkappa$. The generatrix of σ passing through the point A of k^3, is the tangent a to k^3 at A which cuts α in B. Hence C_1 and C_2 coincide in B for any point S of $\varkappa$.

Inversely it appears that an infinite number of lines s correspond to B, the generatrices of k.

Accordingly the representation has one cardinal pair of points, the pair for which C_1 *and* C_2 *coincide in* B. *To this pair there correspond the points of the quadratic cone* $\varkappa$.

If we choose for carrier of this pair of points a definite straight line through B which cuts k^2 besides in K, according to the construction of § 1 there are only ∞^1 image points, which form the generatrix AK of $\varkappa$.

Through making use of the way of producing our representation indicated in § 1, we should perhaps think that the pairs of points (C_1, C_2) for which C_1 lies in B, hence C_2 on the tangent b at B to k^2, are singular. Indeed, for such a pair of points K_1 may be chosen at random on k^2 and K_2 lies in B. There are an infinite number of points C, the points of b. The chord k becomes the tangent a to k^3 at A. If we choose C in B, AC lies along a and we find that any point of a may be considered as the image point of (C_1,C_2).

That this is not right, however, appears if we use the way of producing our representation indicated in § 3. The line s_1 corresponding to the point C_1 lying in B, may be chosen along an arbitrary generatrix of $\varkappa$. The line AC_2 belongs to the plane pencil that has A as vertex and of which the plane is the tangent plane to $\varkappa$ along AB, i. e. the plane of osculation of k^3 at A. The generatrices of this pencil are straight lines of $\Sigma(2,3)$. Hence AC_2 is just the line of the scroll σ that may be derived from C_2 which belongs to Σ, that is the line s_2 corresponding to C_2. This line cuts $\varkappa$ only in A, which point is, therefore, the only image point of all the pairs (C_1,C_2) that are associated relative to k^2 of which one point lies in B.

Hence A is a singular point for our representation. A has this property in common with all the points of k^3. For if we choose S on k^3 we have, instead of two lines s_1 and s_2, a plane pencil of lines s which has S for vertex and which lies in the tangent plane τ to $\varkappa$ at S. The generatrices through A of the scrolls σ corresponding to these lines s, form the plane pencil that has A for vertex and that lies in the plane ABS which cuts α along the line BK, if K is the projection of S on α lying on k^2. For AK is always the generatrix through A of the scrolls ϱ, and accordingly the projections of all the generatrices of the scrolls σ pass through K. But the projections of the generatrices through A of the latter scrolls also pass through B because the projecting planes pass through a. Hence the point S must be considered as the image point of all the pairs of BK that are associated relative to k^2.

Consequently the points of k^3 *are singular for our representation. To* *a point S of k^3 there correspond the pairs of points of the line BK through B that are associated relative to k^2. The pairs of points of which the image lies on k^3, are the ∞^2 of which the carriers pass through B.*

If we choose S in A, there is, besides a plane pencil of lines s, a cone of similar lines, $\varkappa$. Hence the pairs of points (C_1,C_2) of the line b are associated to A, a result already found, on the understanding, however, that the carrier of the coincidence in B may be chosen arbitrarily through that point.

The latter is also true for any point S of k^3 relative to the coincidence in K. This is, for instance, easily seen by the aid of the construction of § 1. If we choose an arbitrary line through K as carrier, the corresponding line k is a chord of k^3 through S. The points K_1, K_2 and C all coincide in K. The image point of the chosen coincidence, i.e. the intersection of k and AC, in fact always lies in S.

The curve k^3 is, therefore, in particular the locus of the image points of the coincidences among the pairs of points that are associated relative to k^2.

§ 5. The most simple systems of ∞^1 pairs of points (C_1, C_2) are the system λ of which all the individuals belong to a given line l of α, and the system π of the pairs of which one point is a given point P of α and the other point may be chosen at random in the polar line p of P relative to k^2.

To all the individuals of a system λ there corresponds the same chord k of k^3, the chord of this curve that does not pass through A of which the projection on α coincides with l. This chord contains the image points of all the pairs of points of λ.

The system λ of the ∞^1 pairs of points of a line l that are associated relative to k^2, are represented on a chord k of k^3.

The points of intersection of k and k^3 are the image points of the coincidences of λ that lie in the points of intersection of l and k^2.

If, in particular, l is a tangent to k^2, the involution defined on l by k^2 becomes parabolic and λ contains only one coincidence. In this case λ is represented on a tangent to k^3.

In § 2 we found:

A system π is represented on a straight line s that touches $\varkappa$ on k^3.

The intersection of s and k^3 is the image point of the pair of points of π of which the carrier passes through B. The two points of intersection outside k^3 of s and the biquadratic surface of the tangents of this curve are the images of the individuals of π for which the point on p lies in one of the points of intersection of p and k^2.

If P is a point of k^2, the system π is at the same time a system λ, (save the indefiniteness of the carrier of the coincidence in the point of contact), and is represented on a tangent to k^3.

§ 6. Of the systems of ∞^2 pairs of points associated relative to k^2, we shall first treat the system Π of the pairs (C_1,C_2) of which the carriers pass through a given point P of α. The straight lines k of these pairs form the scroll of the chords of k^3 that cut AP.

The system Π of the ∞^2 pairs of points the carriers of which pass through a given point P, i. e. a projective inversion with center P and base k^2, is accordingly represented on a quadratic surface Φ through k^3.

Inversely a quadratic surface through k^3 is the image of a similar system, that for which P lies in the point of intersection with α of the line through A of this surface that cuts k^3 only in A.

If P lies on k^2, the image of Π is the cone which projects k^3 out of the point of intersection outside A of AP and k^3.

Two systems Π and Π' corresponding resp. to the points P and P', are represented on two quadratic surfaces Φ and Φ' which, besides k^3, have a chord of this curve in common; it is the image of the system of pairs (C_1,C_2) of the line PP'. Φ and Φ' define a pencil of which each surface is the representation of the system of pairs associated relative to k^2 of which the carriers pass through a given point of PP'.

Let us further investigate the representation of the system Λ of the pairs of which one point lies on a given straight line l. This system consists of the ∞^1 systems π of the points P of l and is, therefore, represented on a surface Ψ which consists of the ∞^1 corresponding lines s. As each of the said systems π contains one individual of the system λ of the pairs (C_1,C_2) of l, Ψ consists of the lines s that cut the chord k of k^3 which corresponds to l.

Ψ has k as nodal line. The two lines s through a point S of k are the images of the systems π for which P lies in one of the two points of the pair (C_1,C_2) that has its image in S. A plane through k contains only one generatrix of Ψ, the line which touches $\varkappa$ in the point of intersection outside k of this plane and k^3. As all the generatrices of Ψ touch the cone $\varkappa$ on k^3, we find:

The system Λ of the ∞^2 pairs of points (C_1,C_2) of which one point lies on a given line l of α, is represented on a cubic scroll Ψ which touches $\varkappa$ on k^3.

The single directrix of Ψ is the line s which represents the system π that is defined by l and the pole of l relative to k^2.

If l is a tangent to k^2, k becomes a tangent to k^3 so that this directrix of Ψ is at the same time a generatrix. In this case Ψ is a scroll of CAYLEY.

A system Π has ∞^1 pairs of points in common with a system Λ, all the carriers of which pass through P and which have one point on l; the conjugated point always lies on the conic corresponding to l in the general inversion with center P and base curve k^2. This system is represented on the intersection different from k^3 of Φ and Ψ, i.e. a cubic (Φ, Ψ) which cuts k^3 in the images of the two coincidences of (Π, Λ) that lie in the points of intersection of l and k^2 and in the image point of the pair of points on the line BP. In the latter image point, the point L corresponding to P, the surface Φ touches the cone $\varkappa$ according to § 2; hence this is also the case for the curve (Φ, Ψ). The two former points of k^3 are the intersections of the chord k corresponding to l and k^3. These are cuspidal points of Ψ; the two corresponding torsal lines are the tangents to k^3 at these points, the images of the systems π of which the point P lies in one of the intersections of l and k^2. As in these cuspidal points of Ψ Φ and Ψ have only the tangent to k^3 as a common tangent, the curve (Φ, Ψ) must touch k^3 at this point.

A system (Π, Λ) *is accordingly represented on a twisted cubic that touches* $\varkappa$ *once on* k^3 *and the latter curve twice.*

If l is the polar line of P relative to k^2, (Π, Λ) consists of the two systems λ corresponding to the tangents to k^2 through P, and of the system π of P. In this case the image consists of two tangents of k^3, and the line touching $\varkappa$ on k^3 which cuts the two said tangents.

The system which is common to two systems Λ and Λ' which correspond to the lines l and l', consists of the system π of the point P that lies in the intersection of l and l', and of the system (Λ, Λ') of the ∞^1 pairs of points associated relative to k^2 of which one point belongs to l and the other to l'. The former system is represented on the line s belonging to Ψ and Ψ' which touches $\varkappa$ on k^3 and cuts k and k'. Besides s and k^3, along which curve Ψ and Ψ' touch each other, these surfaces have a conic (Ψ, Ψ') in common, the image of (Λ, Λ'). As the carriers of (Λ, Λ') envelop a conic, there are two pairs of points of this system the joins of which pass through B, so that the conic (Λ, Λ') cuts the curve k^3 in two points, where it touches $\varkappa$.

Consequently the system of the ∞^1 *pairs of points that have a point on each of two given lines of* α, *is represented on a conic which touches* $\varkappa$ *twice on* k^3.

A check of the latter two results is given by the fact that the class of the envelope of the carriers and the order of the curve of the points of the individuals of a system of ∞^1 pairs of points (C_1, C_2) are resp. equal to the numbers of points of intersection outside k^3 of the image curve with a surface Φ and with a surface Ψ.

§ 7. The pairs of points that are associated to each other relative to k^2 as well as relative to another conic k'^2 of α, form a quadratic involution I, which is represented on a surface X. The class of I, i.e. the number of pairs of I which belong to a straight line l of α, is one. For the points of the pair of I on l are the points of intersection of l with the conic described by C_2 if C_1 moves on l, or the double points of the involution which is defined by the pairs of points lying on k^2 and k'^2. As, accordingly, any line through B contains one pair of points of I, k^3 is a single curve of X. A chord k of k^3 cuts X outside this curve in one point, the image of the pair of points of I which lies on the line l of α corresponding to k. Consequently X is a cubic surface. As the involution I contains one pair of points, of which one point is given, a straight line touching $\varkappa$ on k^3 cuts the surface X only once outside k^3. Hence the surface X must touch k^3 on $\varkappa$.

The involution I has four double points, the points of intersection $Q_1, \ldots, Q_4$ of k^2 and k'^2, which are resp. represented on the corresponding points $P_1, \ldots, P_4$ of k^3. As no line through a point Q_i on which there lies no other point Q_i, contains any pair of I besides the coincidence in Q_i, no chord of k^3 through P_i which does not contain any of the other points P, has any point in common with X outside P_i and k^3. The points $P_1, \ldots, P_4$ are necessarily conical points of X. The lines $Q_i\, Q_k$ are singular for I, as all the pairs of points of $Q_i\, Q_k$ that are associated relative to k^2, are also associated relative to k'^2 and belong, accordingly, to I. The lines $P_i\, P_k$ belong, therefore, all to X.

Consequently a quadratic involution of pairs of points associated relative to k^2, is represented on a surface X that contains four conical points on k^3.

Such a surface may be represented on a plane χ by means of a cubical involution. Through this representation the six lines $P_i\, P_k$ are transformed into the angular points R_{ik} of a complete quadrilateral. A twisted cubic through the points P_i is transformed into a straight line of χ. The diagonals of the said complete quadrilateral are the images of three lines of χ different from $P_i\, P_k$ which cut k^3 once, touch the cone $\varkappa$ in the points of intersection with k^3, and form a triangle. These three lines s are the images of systems π of I of which the points P are singular points of I, to each of which in I the whole polar line relative to k^2 is associated. As each pair of these systems π has a pair of points in common, the points P and the associated straight lines are resp. the angular points and the sides of a polar triangle of k^2. The straight line of X that corresponds to the diagonal $R_{ik} R_{lm}$, cuts the lines $P_i P_k$ and $P_l P_m$ so that the associated system π of I has its point P in the intersection of $Q_i\, Q_k$ and $Q_l\, Q_m$, as it contains one pair of points of each of these lines. The line associated to this point P in I, joins the other two diagonal-points of the complete quadrilateral $Q_1\, Q_2\, Q_3\, Q_4$.

A cubic surface through k^3 which touches $\varkappa$ on k^3, is always the image of such a quadratic involution. For a surface of this kind has one point of intersection with a line s that is not singular so that to a point of α one point is associated in the corresponding involution. Further the surface cuts a conic which touches $\varkappa$ twice on k^3, in two points that are not singular for the representation, so that I contains two pairs of points that have a point on each of two given lines of α, and if a point describes a straight line of α the point associated to it in I describes a conic. I cannot be an inversion relative to k^2, as this is represented on a quadratic surface.

Accordingly a cubic surface through k^3 which touches a quadratic projecting cone of this curve in each point of k^3, has always four conical points on k^3.

If I has a coincidence in B, the quadratic cone $\varkappa$ splits off from X. Consequently I is represented on a plane.

Let us assume besides I an involution I' which is defined by k^2 and a third conic k''^2. I' is represented on a surface X'. The surfaces X and X' define a pencil of cubic surfaces that touch $\varkappa$ on k^3, the image of the pencil of quadratic involutions defined by I and I', of which each individual may be derived from a pencil of conics containing k^2 out of the net defined by k^2, k'^2 and k''^2. The individual of the said pencil of surfaces which passes through a point of $\varkappa$ outside k^3, must degenerate into $\varkappa$ and a plane, as a non-degenerate surface of the pencil cannot have any point in common with $\varkappa$ outside k^3, along which curve it touches $\varkappa$. The corresponding quadratic involution may be derived from the pencil with a base point in B of the net defined by k^2, k'^2 and k''^2.

Hence the intersection of X and X' consists of k^3, counted double, and a plane cubic (X, X') which touches $\varkappa$ in three points on k^3. This curve is the image of the system (I, I') of the pairs of points that are associated relative to k^2, k'^2 and k''^2. As (X, X') has three points that are not singular for the representation in common with a surface Φ as well as with a surface Ψ, the locus of the pairs of points of (I, I') is a cubic, and the carriers of the pairs of (I, I') envelop a curve of the third class. As (X, X') has one point in common with each of the lines of the surfaces of the pencil defined by X and X' which cut k^3 once, the locus of the pairs of (I, I') passes through the singular points of the involutions of the pencil defined by I an I'. Accordingly this locus is the Jacobian of the net defined by k^2, k'^2 and k''^2.

The involution of the pairs of points on the Jacobian of a net containing k^2 which are associated relative to all the conics of the net, is represented on a plane cubic which touches $\varkappa$ three times on k^3.

Besides k^3 three surfaces X, X' and X'' have three points in common on a straight line. This line is the intersection g of the three planes containing the intersections of each pair of the chosen surfaces. The surfaces X, X' and X'' define a net; the degenerate individuals consist of the planes through g and $\varkappa$. A plane through g cuts this net along a pencil of cubics of which three base points lie in the three isolated base points of the net and the remaining six coincide in pairs in the three points of intersection with k^3. A surface Ψ through two of the isolated base points must also pass through the third. For Ψ cuts the plane through g along a cubic which passes through eight base points of the said pencil that lie independently, and which must, therefore, also contain the ninth base point ^{1}).

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1) The independence appears from the fact that through any seven of the base points we can pass a cubic which does not contain the eighth base point. In the first place we can choose the intersection with $\varkappa$ and a straight line through an isolated base point of the net, further the conic through the base points and the line which joins two base points lying on k^3.

Hence the three involutions I, I' and I'' have three pairs of points in common, so that the line which joins a point of one of these pairs to a point of the second, also contains a point of the third. Consequently the common pairs of points of I, I' and I'' form the pairs of opposite angular points of a complete quadrilateral. If I, I' and I'' are defined, besides by k^2, resp. by k'^2, k''^2 and k'''^2, these pairs of points are associated relative to all the conics of the linear system defined by $k^2, \ldots, k'''^2$.

In this way we have found a proof of the theorem that the pairs of points which are associated relative to all the conics of a complex, are the pairs of opposite angular points of a complete quadrilateral.

§ 8. A plane V of points S is the image of a system of ∞^2 pairs of points (C_1, C_2). As V has resp. one, one and two points in common with a line s, a chord k and a conic which touches $\varkappa$ twice on k^3, we may conclude that to V there corresponds a quadratic involution of pairs of points associated relative to k^2. This involution has a coincidence in B, because V cuts all the generatrices of $\varkappa$. It may be derived from a pencil of conics containing k^2 which has a base point in B.

A plane is the image of a quadratic involution of pairs of points associated relative to k^2 which has a coincidence in B.

The six singular lines of the involution are represented on the points of intersection of V and k^3 and on the three chords of this curve in V. The three systems π each of which is defined by a singular point of the involution and the polar line associated to it, correspond to the three lines in V which touch $\varkappa$ on k^3. A surface Ψ cuts V along a cubic which touches $\varkappa$ in the three points of intersection with k^3, the image of the correspondence between the points of a straight line and the conic associated to it through the involution, which, as the said cubic cuts any line s in V once outside k^3, passes through the singular points of the involution.

To a plane through A as well as to an arbitrary tangent plane to k^3 there corresponds an involution with two coinciding coincidences, etc.

As a special case let us choose for V a tangent plane to $\varkappa$. We can consider V as consisting of lines s which form a plane pencil the vertex of which lies in the point where V touches the curve k^3. Accordingly the associated system is formed by the systems π that have their point P on a straight line of α through B; it is, therefore, a system Λ. A tangent plane to $\varkappa$ forms with $\varkappa$ a degeneration of a surface Ψ.

Consequently the system of the pairs of points of which one point lies on a straight line through B, is represented on a tangent plane to $\varkappa$.

In particular the plane of osculation to k^3 at A is the image of the system of the pairs of which one point lies on the tangent b to k^2 at B.

The points S of a line g in space are the images of the pairs (C_1, C_2) of a system γ of ∞^1 pairs of points that are associated relative to k^2.

As g cuts a surface Φ and a surface Ψ resp. twice and three times, the carriers of γ envelop a conic and the locus of the pairs of γ is a cubic. This curve has a node in B. For γ contains two coincidences lying in B, the carriers of which are the lines through B which cut the generatrices of $\varkappa$ meeting g, on k^2. The system γ consists of the common pairs of points of the pencil of quadratic involutions which is represented on the pencil of planes of which g is the axis, hence of the pairs of points that are associated relative to all the conics of a net that has a base point in B. From the curve of the third class which is enveloped by the carriers of a general net, there splits off the plane pencil that has B for vertex.

Accordingly a line g is the image of the involution defined by a net of conics containing k^2 that has its base point in B, on its Jacobian.

The lines k corresponding to the carriers of γ, are the chords of k^3 which cut g. They form ∞^1 triangles inscribed in k^3, to which there correspond triangles inscribed in k^2 the sides of which are carriers of γ.

Consequently the conic enveloped by the carriers of γ, is inscribed in k^2, hence also in all the conics of the net from which γ is derived.

The lines g of a plane V are the images of systems γ of the quadratic involution I corresponding to V. The loci of the pairs of points of these systems γ are cubics which are *invariant* for I. They have a node in B, pass through the three singular points of I, and cut the singular lines of I which does not pass through B, in a pair of points that are associated relative to k^2. There are *four* systems of such cubics that are invariant for I.

A line g that cuts k^3 once, has resp. one and two points which are not singular for the representation, in common with a surface Φ and a surface Ψ. Accordingly the locus of the pairs of points of the corresponding system γ is a conic and the carriers of γ form a plane pencil. From the system γ corresponding to an arbitrary line g, also the involution has split off which is defined through k^2 on a straight line through B, and the system of pairs of points of which the carriers form the plane pencil that has for vertex the projection of the point of intersection of g and k^3.

To a line cutting k^3 once, there correspond, accordingly, a conic and a plane pencil. The conic passes through B, as γ contains a coincidence in this point, which is represented on the point of intersection outside k^3 of g and $\varkappa$. The vertex of the plane pencil is the center of an inversion which is represented on the quadratic surface Φ of the chords of k^3 cutting g, and through which the conic is transformed into itself.

From this it appears that the generatrices of a quadratic surface Φ corresponding to a point P of α that cut k^3 once, are associated to the conics through B which are invariant for an inversion with center P and base curve k^2.

As γ has two coincidences, one in B and one in the point of k^2 that corresponds to the point of intersection of g and k^3 [1]), we find:

The Jacobian of a net of conics containing k^2 which has two base points one of which lies in B, degenerates into the line joining these base points and a conic through the base points. The involution defined on the conic by the net, is represented on a line that cuts k^3 once.

The three plane pencils in a plane V of lines which cut k^3 once, give three systems of conics that are invariant for the involution I corresponding to V. Such a system consists of the conics passing through B and another double point of I as well as through the two singular points which do not lie on the side of the two said double points and which contain a pair of points associated relative to k^2, on the side through the angular points of which the conics do not pass.

In all, six systems of this kind correspond to I. The other three are represented on conics which pass through the points of intersection of k^3 and V and which, besides, touch $\varkappa$ in the point of intersection of k^3 and V corresponding to the double point of I through which the conics of such a system do not pass [2]).

A line g through A is the image of the system of the ∞^1 pairs of points associated relative to k^2, of the two straight lines through B, BK_1 and BK_2, if K_1 and K_2 are the points of contact of the tangents to k^2 through the point of intersection C of g and α. From the system associated to an arbitrary line g there splits off besides the parabolic involution which is defined by k^2 on the tangent b at B. The corresponding net of conics has two base points which coincide in B.

The Jacobian of a net with two base points that coincide in B, degenerates into the common tangent of the conics of this net and into two straight lines through B. The system of the pairs of points associated relative to the net of which each of the latter two lines contains one point, is represented on a straight line through A.

If g is a chord k of k^3, the corresponding net has three base points one of which lies in B. The Jacobian degenerates into the line l of α which corresponds to k that joins the base points different from B, and into the two lines which may be drawn through B and the other two base points, which lines are associated to the points of intersection of k and k^3.

To a straight line g that touches $\varkappa$ on k^3, there corresponds a net with two base points for which the Jacobian has degenerated into the join of these base points, counted double, and into the line p of the system π which is represented on the said straight line. The net associated to a tangent of k^3, has a base point in B and two coinciding base points outside B. The Jacobian degenerates into the common tangent and into the line joining the point of contact and B, counted double.

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[1]) Cf. § 9, par. 2.

[2]) Cf. § 9.

§ 9. A curve k^n is the image of a system γ of ∞^1 pairs of points that are associated relative to k^2. We suppose that k^n touches $\varkappa$ p_1 times on k^3 outside A, and cuts k^3 besides p_2 times outside A.

If a system γ has a pair of points on a straight line through B, the image curve cuts k^3. If the image S on the image curve approaches the point of intersection with k^3, the chord of k^3 through S approaches the line joining the said point of intersection to A. In this case the image curve must touch $\varkappa$ on k^3. A point where the image curve cuts k^3 but does not touch $\varkappa$, is consequently the image of a coincidence of γ, and to a point where the image curve touches k^3, there corresponds a double coincidence of γ, which, however, only forms a single pair of this system.

The class of the system γ which is represented on k^n, i. e. the class of the envelope of the carriers of γ, is equal to the number of points of intersection of k^n and a surface Φ that are not singular for the representation, hence: $2n-p_1-p_2$, and the order, i. e. the order of the locus of the pairs of points of γ, is equal to the number of points of intersection of k^n and a surface Ψ that are not singular for the representation, hence to $3n-2p_1-p_2$. As k^n cuts the cone $\varkappa$ outside k^3 in $2n-2p_1-p_2$ points, γ has $2n-2p_1-p_2$ coincidences in B, and accordingly the locus of the pairs of points of γ has a $2n-2p_1-p_2$-fold point in B.

A curve k^n of the order n which touches $\varkappa$ p_1 times on k^3 outside A, and which besides cuts k^3 p_1 times outside A, is the image of a system γ of ∞^1 pairs of points associated relative to k^2 of the class $2n-p_1-p_2$ and of the order $3n-2p_1-p_2$ which has $2n-2p_1-p_2$ coincidences in B.

The number of the coincidences of γ outside B is p_2.

Let us now investigate the representation of a system γ of ∞^1 pairs of points associated relative to k^2 of the class μ and the order ν that does not have any coincidence in B and does not contain either any pair associated relative to k^2 which belongs to the tangent b at B to k^2. The latter two conditions can be satisfied by a system γ of any kind.

As the image curve of γ does not pass through A, we find by solving n, p_1, and p_2 out of the equations

$$2n-p_1-p_2=\mu$$

$$3n-2p_1-p_2=\nu$$

$$2n-2p_1-p_2=0:$$

The image of a system γ of ∞^1 pairs of points associated relative to k^2 of the class μ and of the order ν that does not contain any pair of which one point lies in B, is a curve of the order ν which touches $\varkappa$ μ times on k^3 outside A and which besides cuts k^3 $2(\nu-\mu)$ times outside A.

Hence the order of a system of ∞^1 pairs of points associated relative to k^2, is always greater than or equal to the class.

Further:

A system of ∞^1 pairs of points associated relative to k^2 of the order ν and the class μ contains $2(\nu-\mu)$ coincidences.

A surface Ω of the order r which contains s leaves through k^3 touching $\varkappa$ on k^3 and of which t more leaves pass through k^3, is the image of a system Γ of ∞^2 pairs of points associated relative to k^2. We suppose that A as well as any point of k^3 is an $(s+t)$-fold point of Ω.

The order of Γ, i.e. the number of pairs of this system of which one point lies in a given point of α, hence the number of points of intersection of Ω with a straight line s which touches $\varkappa$ on k^3, that are not singular for the representation, is $r-2s-t$ and the class, i.e. the number of pairs of Γ that belong to a given straight line of α, hence the number of non-singular points of intersection of Ω and a chord k of k^3, is equal to $r-2s-2t$. As each generatrix of $\varkappa$ cuts the surface Ω in $r-3s-2t$ non-singular points, Γ has an $r-3s-2t$-fold full coincidence in B, i.e. a coincidence of which the carrier is indefinite and which forms an $r-3s-2t$-fold pair of points of Γ.

A surface Ω of the order r containing s leaves through k^3 which touch $\varkappa$ on k^3, and which has t more leaves through k^3 and an $(s+t)$-fold point in A, is the image of a system of ∞^2 pairs of points associated relative to k^2 of the order $r-2s-t$ and of the class $r-2s-2t$ that has an $(r-3s-2t)$-fold full coincidence in C.

The conic k^2 is a t-fold curve of coincidence for Γ.

The pairs of Γ define an involutorial correspondence $(r-2s-t, r-2s-t)$. If a point describes a straight line of α, the points corresponding to it in this involutorial correspondence describe a curve of which the order is equal to the number of non-singular points of intersection of Ω with the image of the system of the ∞^1 pairs of points associated relative to k^2 which have a point on each of two given straight lines of α, i.e. according to § 6 or according to the second theorem of this § a conic which touches $\varkappa$ twice on k^3. For the order of the curve associated to a straight line, we find therefore $2r-4s-2t$.

Inversely we investigate the representation of a system Γ of the order ϱ and of the class σ that has no full coincidence in B. The latter condition may again be satisfied by a system Γ of any kind. A straight line of α through B contains as many pairs of points non-singular for the representation and different from the coincidence in B, as an arbitrary line of α. A chord of k^3 through A must cut Ω outside A in as many points as a chord through an arbitrary point P of k^3 has in common with Ω outside P, so that A and P are points of the same multiplicity for Ω.

We may, therefore, find the characteristic numbers r, s and t of Ω by solving them out of the equations:

$$\begin{aligned} r-2s-t&=\varrho \\ r-2s-2t&=\sigma \\ r-3s-2t&=0. \end{aligned}$$

We find:

A system Γ of the order ϱ and of the class σ that has no full coincidence in B, is represented on a surface Ω of the order $2\varrho+\sigma$ which contains σ leaves through k^3 touching $\varkappa$ on k^3, which has, besides, $\varrho-\sigma$ leaves through k^3, and which contains a ϱ-fold point in A.

Accordingly the order of a system Γ is always greater than the class.

For a system of ∞^2 pairs of points associated relative to k^2 of the order ϱ and of the class σ, k^2 is a $(\varrho-\sigma)$-fold curve of coincidence. For $2\varrho-\varrho-\sigma=\varrho-\sigma$ of the points of intersection outside k^3 of an arbitrary straight line s touching $\varkappa$ on k^3 lie on k^3 if we choose for s a tangent to this curve.

The order of the curve which in the involution defined by Γ is associated to a straight line, is equal to the number of non-singular points of intersection of Ω and a conic which touches $\varkappa$ twice on k^3; hence it is equal to 2ϱ.

§ 10. A system γ of ∞^1 and a system Γ of ∞^2 pairs of points associated relative to k^2, have as many pairs in common as the image curve of γ and the image surface of Γ have points of intersection that are not singular for the representation. If the class and the order of γ are resp. μ and ν, the class and the order of Γ resp. ϱ and σ, we find for the number of the points of intersection in question:

$$\nu(2\varrho+\sigma)-\mu(2\sigma+\varrho-\sigma)-2(\nu-\mu)\varrho=\mu\varrho-\mu\sigma+\nu\sigma.$$

A system of ∞^1 pairs of points associated relative to k^2 of the class μ and the order ν has

$$\mu(\varrho-\sigma)+\nu\sigma$$

pairs in common with a system of ∞^2 similar pairs of the order ϱ and the class σ.

The intersection (Ω,Ω') different from k^3 of the surfaces Ω and Ω' which represent two systems $\Gamma(\varrho,\sigma)$ and $\Gamma'(\varrho',\sigma')$, is of the order:

$$(2\varrho+\sigma)(2\varrho'+\sigma')-3\varrho\varrho'-3\sigma\sigma'=\varrho\varrho'+2\varrho\sigma'+2\sigma\varrho'-2\sigma\sigma'.$$

The curve which Ω has in common with a surface Φ, cuts each chord of k^3 on this surface in σ points, each straight line of Φ cutting k^3 once, in $\varrho+\sigma$ points, and it is accordingly a curve $(\sigma,\varrho+\sigma)$ of this quadratic surface. According to a well known theorem this curve has

$$\sigma(\varrho'+\sigma')+\sigma'(\varrho+\sigma)=\varrho\sigma'+\sigma\varrho'+2\sigma\sigma'$$

points in common with the curve $(\sigma',\varrho+\sigma')$ along which Ω' cuts Φ outside k^3.

According to § 2 Φ touches the cone $\varkappa$ in one point of k^3, hence also σ leaves of Ω and σ' leaves of Ω'. The curves of intersection different from k^3 of Ω and Φ and of Ω' and Φ have resp. a σ- and a σ'-fold point in this point of k^3; they cut each other, therefore, outside k^3 in

$$\varrho\sigma' + \sigma\varrho' + \sigma\sigma'$$

points.

These are the points of intersection outside k^3 of the curve (Ω, Ω') and Φ. Hence in all (Ω, Ω') cuts the curve k^3 in

$$2\,(\varrho\varrho' + 2\varrho\sigma' + 2\sigma\varrho' - 2\sigma\sigma') - \varrho\sigma' - \sigma\varrho' - \sigma\sigma' = 2\,\varrho\varrho' + 3\,\varrho\sigma' + 3\,\sigma\varrho' - 5\sigma\sigma'$$

points.

If we choose Γ and Γ' so that the system common to these systems does not contain any pair of which one point lies in B, the curve (Ω, Ω') does not pass through A, nor does it cut the cone $\varkappa$ outside k^3. The points of intersection outside k^3 of (Ω, Ω') and an arbitrary quadratic surface through k^3, must lie on k^3 if we choose the cone $\varkappa$ for this surface.

Consequently (Ω, Ω') touches the cone $\varkappa$ in $\varrho\sigma' + \sigma\varrho' + \sigma\sigma'$ points on k^3, and cuts this curve besides in $2\,\varrho\varrho' + 2\,\varrho\sigma' + 2\,\sigma\varrho' - 6\,\sigma\sigma'$ points.

We find therefore by the aid of the first theorem of § 9:

Two systems Γ (ϱ, σ) and Γ' (ϱ', σ') have in common a system of ∞^1 pairs of points associated relative to k^2 of the class $\varrho\sigma' + \sigma\varrho' + \sigma\sigma'$ and of the order $\varrho\varrho' + 2\varrho\sigma' + 2\sigma\varrho' - 2\sigma\sigma'$.

If we determine the number of non-singular points of intersection of (Ω, Ω') with the image surface of a third system Γ'' (ϱ'', σ''), we find:

Three systems Γ (ϱ, σ), $\Gamma'(\varrho'\sigma)$ and Γ'' (ϱ'', σ'') have

$$\varrho\varrho'\sigma'' + \varrho\sigma'\varrho'' + \varrho\sigma'\sigma'' + \sigma\varrho'\varrho'' + \sigma\varrho'\sigma'' + \sigma\sigma'\varrho'' - 3\sigma\sigma'\sigma''$$

pairs of points in common.

Mathematics. — *"On Derived Functions of a Real Variable."* By Prof. J. Wolff. (Communicated by Prof. R. Weitzenböck.)

(Communicated at the meeting of February 28, 1925.)

1. In the Proc. of the London Math. Society, serie 2, vol. 9, 1911, p. 360—368, W. H. Young gives a number of sufficient conditions under which the product of a derived function f' and a function Φ is again a derived function.

In this paper we give a few extensions of Young's theorems and we show by an example that we cannot expect any progress worth mentioning in this train of thought (theorem C).

2. We shall prove the following theorems:

A. *If f' is summable and if Φ has finite derived numbers, $f'\Phi$ is a derivative.*

This theorem is an extension of the following theorem of Young: "if f' is the derivative of a function of limited variation and Φ has a finite summable derivative, $f'\Phi$ is a derivative."

B. *If f' is limited, Φ approximately continuous and limited, $f'\Phi$ is a derivative."*

This is an extension of Young's theorem:

"If f' is limited and Φ is continuous, $f'\Phi$ is a derivative".

C. *There are summable derivatives f' with only one point of discontinuity, and continuous functions Φ so that $f'\Phi$ is no derivative.*

3. In order to prove A and B we remark that in both cases f' and Φ are summable so that if a is a point in the interior of the interval where f' and Φ are given, we may put

$$\psi(x)=\int_a^x f'\Phi.$$

If x_0 is another point in the interior of the interval and if the same holds good for x_0+h, we have

$$\frac{1}{h}\left\{\psi(x_0+h)-\psi(x_0)\right\}=\frac{1}{h}\int_{x_0}^{x_0+h} f'\Phi=\frac{\Phi(x_0)}{h}\int_{x_0}^{x_0+h} f'+\frac{1}{h}\int_{x_0}^{x_0+h}\{\Phi-\Phi(x_0)\}f'=$$

$$=\Phi(x_0)\,\frac{f(x_0+h)-f(x_0)}{h}+\frac{\theta}{h}\int_{x_0}^{x_0+h}|\Phi-\Phi(x_0)|\,.\,|f'| \quad ; \quad |\theta|<1 \;. \qquad (1)$$

The first term of (1) $\to 0$ for $h \to 0$.

In case A we have

$$|\Phi - \Phi(x_0)| < K\,|h|,$$

where K can vary with x_0 but does not depend on h. Hence the absolute value of the second term of (1) is less than that of $K\int_{x_0}^{x_0+h} |f'|$, and, f' being summable, this integral has zero as limit for $h \to 0$. In this way we have proved that $\Phi(x_0)\,f'\,(x_0 = \Psi'(x_0)$.

4. In case B we choose a positive number ε and divide the interval $I(x_0, x_0 + h)$ into the two sets of points I_1 containing the points where $|\Phi - \Phi(x_0)| < \varepsilon$ and I_2 containing the points where $|\Phi - \Phi(x_0)| \geqq \varepsilon$. If μI_2 is the measure of I_2, the approximative continuity of Φ means:

$$\frac{1}{h}\,\mu I_2 \to 0 \quad \text{for} \quad h \to 0 \,. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

If M is the upper limit of $|f'|$ we have

$$\frac{1}{|h|}\int_{I_1} |\Phi - \Phi(x_0)|\,.\,|f'| \leqq \frac{\varepsilon}{|h|}\int_{I_1} |f'| \leqq \frac{\varepsilon M}{|h|}\,\mu I_1 \leqq \varepsilon M \quad . \quad . \quad (3)$$

If N is the upper limit of $|\Phi|$ we have

$$\frac{1}{|h|}\int_{I_2} |\Phi - \Phi(x_0)|\,.\,|f'| \leqq \frac{2MN}{|h|}\,\mu I_2 \to 0 \quad \text{for} \quad h \to 0 \,. \quad . \quad (4)$$

According to (3) and (4) the second term of (1) has the limit zero for $h \to 0$, hence $\Phi(x_0)\,f'(x_0) = \psi'(x_0)$.

5. In order to prove theorem C we consider the function

$$f(x) = \int_0^x |t|^{-\frac{1}{2}} \sin\frac{1}{t}\,dt.$$

For $x \neq 0$ we have

$$f'(x) = |x|^{-\frac{1}{2}} \sin\frac{1}{x} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Further for $x \neq 0$

$$\left|\frac{f(x) - f(0)}{x}\right| = \frac{1}{|x|}\left|\int_0^x |t|^{-\frac{1}{2}} \sin\frac{1}{t}\,dt\right| = \frac{1}{|x|}\left|\int_0^{|x|} t^{-\frac{1}{2}} \sin\frac{1}{t}\,dt\right| =$$

$$= \frac{1}{|x|}\left|\int_{\frac{1}{x}}^{\infty} u^{-\frac{3}{2}} \sin u\,du\right|.$$

By applying the second theorem of the mean we find

$$\left|\frac{f(x)-f(0)}{x}\right| = |x|^{\frac{1}{2}} \left| \int_{\frac{1}{|x|}}^{\xi} \sin u \, du \right| < 2\,|x|^{\frac{1}{2}} \to 0 \text{ for } x \to 0. \quad . \quad . \quad (6)$$

From (5) and (6) follows

$$f'(x) = |x|^{-\frac{1}{2}} \sin \frac{1}{x} \quad , \quad x \neq 0,$$

$$f'(0) = 0.$$

From $|f'| < |x|^{-\frac{1}{2}}$, $x \neq 0$ it follows that f' is summable.

Further $x = 0$ is the only point of discontinuity of f'.
If we consider the continuous function

$$\Phi(x) = |x|^{\frac{1}{2}} \sin \frac{1}{x} \quad , \quad x \neq 0$$

$$\Phi(0) = 0,$$

we have

$$\left.\begin{aligned} f'(x)\,\Phi(x) &= \sin^2 \frac{1}{x} \quad , \quad x \neq 0 \\ f'(0)\,\Phi(0) &= 0 \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (7)$$

Be $F(x) = \int\limits_0^x f'(t)\,\Phi(t)\,dt = \int\limits_0^x \sin^2 \frac{1}{t}\,dt.$

For $x \neq 0$ we have

$$F'(x) = \sin^2 \frac{1}{x} = f'(x)\,\Phi(x) \quad . \quad . \quad . \quad . \quad . \quad . \quad (8)$$

Further for $\frac{1}{k\pi} < |x| \leqq \frac{1}{(k-1)\pi}$, k integer and $\geqq 2$:

$$\frac{F(x)-F(0)}{x} = \frac{1}{x}\int\limits_0^x \sin^2 \frac{1}{x}\,dx = \frac{1}{|x|}\int\limits_0^{|x|} \sin^2 \frac{1}{t}\,dt > (k-1)\,\pi \int\limits_0^{\frac{1}{k\pi}} \sin^2 \frac{1}{t}\,dt =$$

$$= (k-1)\,\pi \int\limits_{k\pi}^{\infty} \frac{\sin^2 u\,du}{u^2} = (k-1)\,\pi \sum_{n=k}^{\infty} \int\limits_{n\pi}^{(n+1)\pi} \frac{\sin^2 u\,du}{u^2} >$$

$$> (k-1)\,\pi \sum_{n=k}^{\infty} \frac{1}{(n+1)^2\,\pi^2} \int\limits_0^{\pi} \sin^2 u\,du = \frac{k-1}{2} \sum_{n=0}^{\infty} \frac{1}{(n+1)^2} > \frac{k-1}{2\,(k+1)}.$$

And

$$\frac{F(x)-F(0)}{x} < k\pi \int\limits_{0}^{\frac{1}{(k-1)\pi}} \sin^2 \frac{1}{t}\, dt = k\pi \int\limits_{(k-1)\pi}^{\infty} \frac{\sin^2 u\, du}{u^2} =$$

$$= k\pi \sum_{n=k-1}^{\infty} \int\limits_{n\pi}^{(n+1)\pi} \frac{\sin^2 u}{u^2} < k\pi \sum_{n=k-1}^{\infty} \frac{1}{n^2\pi^2} \int\limits_{0}^{\pi} \sin^2 u\, du = \frac{k}{2} \sum_{n=k-1}^{\infty} \frac{1}{n^2\pi^2} < \frac{k}{2(k-2)} .$$

For $x \rightarrow 0$ we have $k \rightarrow \infty$, hence

$$F'(0) = \frac{1}{2} \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad (9)$$

From (8) and (9) follows that F has everywhere a derivative, to wit $\sin^2 \frac{1}{x}$ for $x \neq 0$ and $\frac{1}{2}$ for $x = 0$.

If now $f'\Phi$ were a derivative, $F' - f'\Phi$ would also be a derivative, these functions being finite. But according to (7), (8) and (9) $F' - f'\Phi = 0$ for $x \neq 0$ and $= \frac{1}{2}$ for $x = 0$; consequently this function is no derivate.

$f'\Phi$ is, therefore, no derivative (although its integral F has a limited derivative). As f' is summable, has only one point of discontinuity, and Φ is continuous, we have proved theorem C.

Utrecht, Jan. 12, 1925.

Chemistry. — *„Decomposition of Paraffin Wax at 450° C. in Presence and in Absence of Hydrogen under High Pressure."* By Prof. H. I. WATERMAN and J. N. J. PERQUIN, chem. eng. (Communicated by Prof. J. BÖESEKEN).

(Communicated at the meeting of February 28, 1925.)

Earlier investigations have shown the favourable influence of hydrogen under high pressure on the process of decomposition which occurs when paraffin wax is heated to 450° C. It was found that hydrogen under high pressure:

a. Enters into combination, and forms part of the products, during the reactions which are proceeding.

b. Causes the production of less unsaturated distillates (gasoline and kerosene).

c. Lowers the specific gravity of the residue obtained on distillation of the reaction-product.

Notwithstanding the lack of experimental data and our imperfect knowledge of the reactions which occur, we have been successful in adding to our knowledge of the Berginisation process. We have reached this result by studying the influence of time on the decomposition at 450° C. of paraffin wax in the presence and in the abcence of hydrogen under high pressure. The raw material which was used in these experiments was Rangoon paraffin, solidifying point (SHUKOFF) 58°, specific gravity 20°/4°: 0.913. Elementary analysis gave 84.6 per cent. C. and 14.8 per cent. H. The charge for each experiment was 200 grams; this was heated at 450° C. in the autoclave already described by us [1]). To promote mixing, three steel balls of a total weight of 79.5 grams were added. The chief results are shown in the appended table.

The Influence of Time on the Decomposition of Paraffin Wax at 450° C. without the Addition of Hydrogen („Cracking").

The quantity of gas produced and the maximum pressure reached increase with time of heating; the pressure after cooling and the volume of gas obtained likewise increase. The volume of „heavy hydrocarbons" also increases to a determined limit and in experiment 92 this maximum is reached. The quantity of hydrogen liberated increases regularly, while the average number of atoms of carbon per molecule of the methane hydrocarbons obtained does not show much variation; it decreases from 2.4 to 2.1. Only traces of coke are formed at first. After two hours

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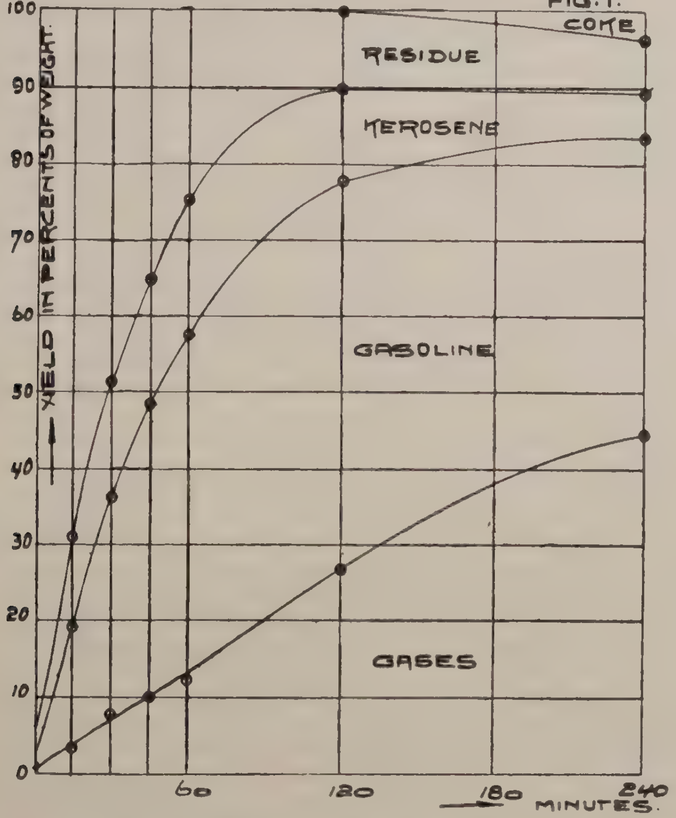
[1]) Journ. of the Institution of Petrol. Technologists, Vol. 10, N^0. 45, Sept. 1924, p. 671—672. These Proceedings 27, p. 83 (1923—24).

(experiment 92) 0.3 per cent. of ,,carbon" is found ; but, after 4 hours, this has increased to 4.0 per cent. in the case of experiment 94. Our experiments indicate that the process is a normal one ; the paraffin hydrocarbons break down, immediately forming decomposition products such at the lower hydrocarbons (ethane and probably methane), and hydrogen. Since the liberation of ,,carbon" is not immediate, but takes place subsequently with great rapidity, it must do so at the expense of the products of decomposition, and not of the hydrocarbons present in the unaltered paraffin wax itself. The oil produced by short periods of heating solidifies completely at ordinary temperatures, while with longer periods the product becomes more liquid, notwithstanding the formation of considerable quantities of gas. At first the specific gravity diminishes rapidly, until after about one hour's heating the minimum is reached (No. 89, 0.767 ; No. 92, 0.766). Thereafter the liberation of ,,carbon" begins and at the same time the specific gravity of the oil rises (No. 94, 0.777).

,,CRACKING" (450°C) OF PARAFFIN WAX.
YIELD IN PERCENTS OF WEIGHT.

FIG. 1.



The liquid product becomes progressively richer in gasoline although the absolute yield of gasoline (Fig. 1) after a rapid initial increase diminishes after two hours (after 2 hours, 50.6 per cent. ; after 4 hours, 38.9 per cent).

The percentage of kerosene in the liquid product diminishes after the first hour, as does the percentage yield (Fig. 1). The quantity of residue boiling above 300° C. diminishes continuously with the percentage yield (Fig. 1).

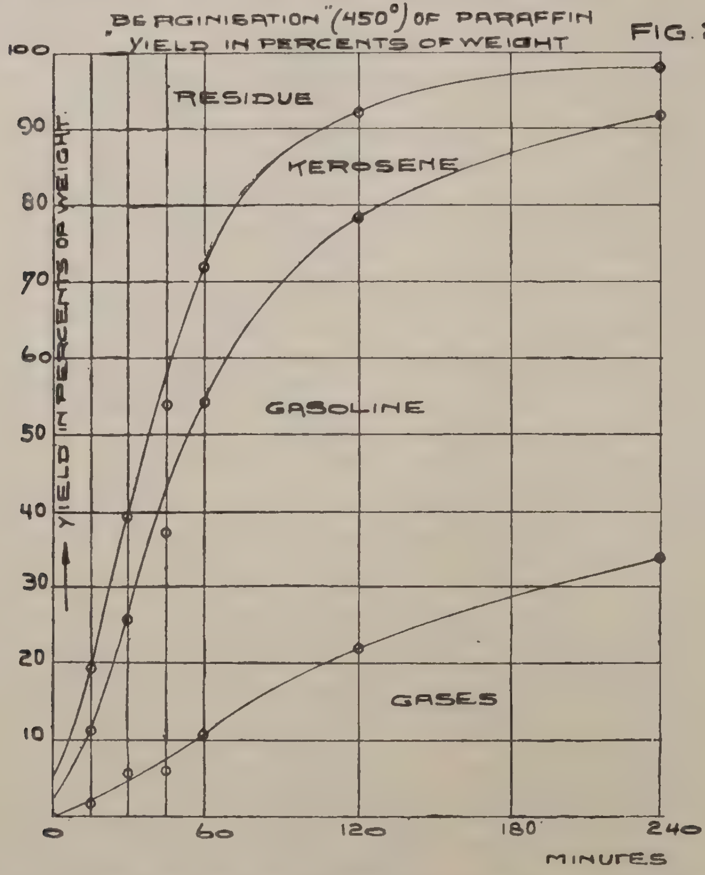


FIG. 2

These facts show that at first gas, gasoline and kerosene increase at the expense of the residue, but that subsequently the kerosene and gasoline at first formed diminish with the residue. As a result it is only the yield of gas which increases, with accompanying liberation of ,,carbon". It must be understood that none of the fractions mentioned remains unaltered during the process. The whole system, excluding such constituents as hydrogen and methane, is in a condition of continual decomposition. This is proved by the decrease in the bromine values of the oil produced (7.5, 19.6, 25.1, 27.5, 27.4, 23.0, and 17.5 after 1, 15, 30, 45, 60, 120 and 240 minutes respectively). This decrease occurs after a preliminary increase (Fig. 3). The quantity of heavy hydrocarbons in the gas at first rises, but after two hours begins to fall, with an accompanying decline in the bromine value. The lowering of the bromine value is probably not due to the formation of gaseous unsaturated products such as ethylene, but rather to the occurrence of polymerisation. In this connection it is interesting to note that the specific gravity of the residue from the oil produced by cracking decreases at first, and afterwards increases rapidly, finally becoming greater than unity (Fig. 4). It has already been mentioned that the specific gravity of the liquid product of the cracking experiments rises with prolonged treatment (Fig. 4).

The Influence of Time on the Decomposition at 450° C. of Paraffin Wax in the Presence of Hydrogen under High Pressure (Bergius Process).

In these experiments the autoclave was charged with hydrogen to 110 kg per sq. cm. before heating. The maximum pressures reached indicate a course of events different from that obtained in the cracking experiments. The maximum pressures 210.5 and 218 kg. per sq. cm. in experiments 99 and 106 are apparently caused merely by the rise in temperature, for decomposition and liberation of gas have hardly begun. Experiments 103,

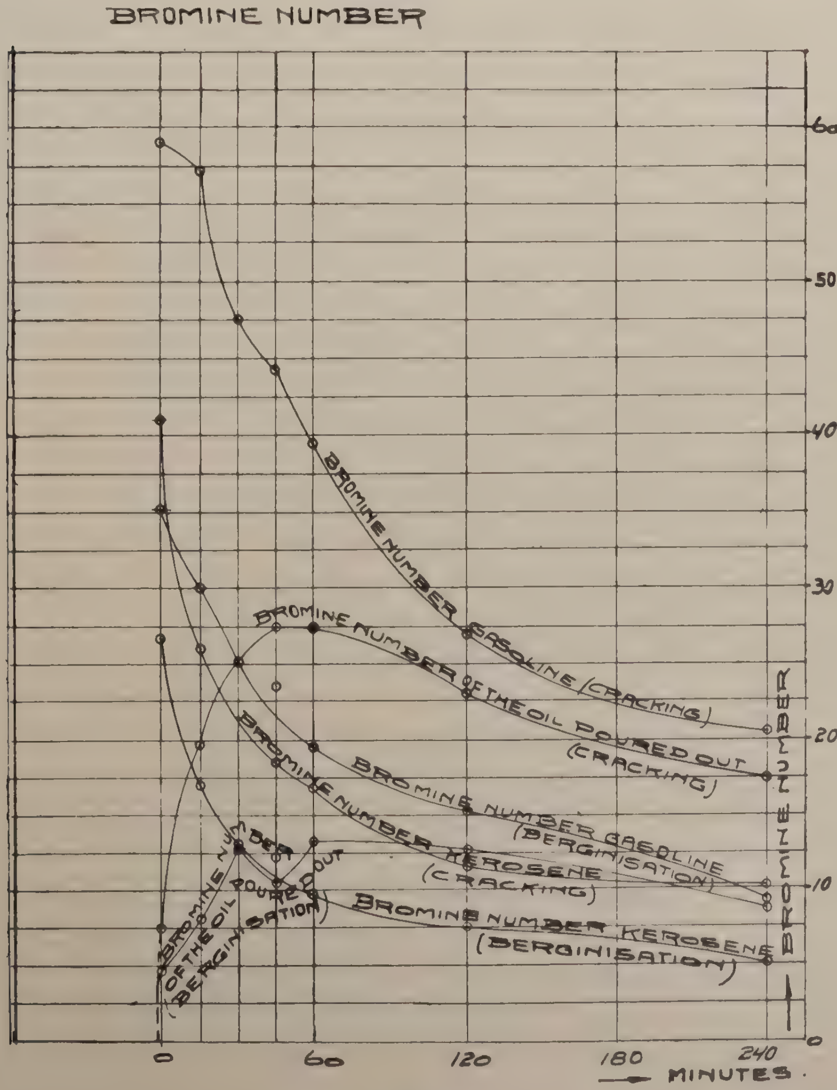


Fig. 3.

N⁰.	Readings during the experiment						Ingoing Material			Product (per cent. on wax charged)				Analysis of			
															Eng		
															Per cent. by weight liquid product		
	Time to reach reaction temp. (min.)	Time at reaction temp. (min.)	Initial pressure (kg. per sq. cm.)	Maximum pressure (kg. per sq. cm.)	Pressure cold (kg. per sq. cm.)	Temperature during reaction (° c.)	Wax (g.)	Gas (g)	Gas (per cent. on wax).	Oil	Gas	„Carbon"	Loss (calculated)	Specific gravity	Gasoline to 220° c.	Kerosene 220—300° c.	Residue above 300° c.
99	25	1	110	210.5	105	450°	200	11.4	5.7	99.7	6.1	0		—	—	—	—
106	29	1	110	218		450°	200	12.7	6.3	99.7	6.6			—	2.3	2.4	94.8
107	**26**	**1**	**0**	**6.2**	**0.6**	**450°**	**200**	**0**	**0**	**99.3**	**0.7**			**0.884**	**2.5**	**2.9**	**94.2**
103	23	15	110	220	106.5	450°	200	12.4	6.2	98.5	7.7			—	9.3	8.4	81.7
108	**30**	**15**	**0**	**16.3**	**2.7**	**450°**	**200**	**0**	**0**	**96.8**	**2.2**		**1.0**	**0.831**	**15.1**	**12.2**	**71.4**
104	30	30	110	223	104	450°	200	12.7	6.3	94.5	9.2		2.6	0.819	20.3	14.3	64.2
109	**25**	**30**	**0**	**28.4**	**4.8**	**450°**	**200**	**0**	**0**	**92.5**	**4.3**		**3.2**	**0.781**	**28.2**	**16.3**	**52.8**
102	26	45	110	219	100	450°	200	12.7	6.3	94.3	9.2		2.8	0.755	30.6	18.0	48.8
111	**39**	**45**	**0**	**37**	**6.2**	**450°**	**200**	**0**	**0**	**90.0**	**6.7**		**3.3**	**0.771**	38.5	**18.3**	**39.2**
74	28	60	110	224	95	450°	200	11.6	5.8	89.5	14.2	0	2.1	0.741	46.9	19.7	29.6
76	36	60	110	222	96	450°	200	11.5	5.8	89.5	13.1		3.2	0.746	44.5	19.8	33.5
89	**28**	**60**	**0**	**48**	**8**	**450°**	**200**	**0**	**0**	**87.7**	**11.0**		**1.3**	**0.767**	**47.9**	**19.9**	**28.8**
80	30	120	110	223	85.5	450°	200	11.6	5.8	78.0	22.2	0	5.6	0.718	67.8	17.5	10.0
78	32	60	110	228	85	*460°*	200	11.6	5.8	77.0	23.7		5.1	0.719	69.0	16.9	9.5
92	**25**	**120**	**0**	**68**	**16**	**450°**	**200**	**0**	**0**	**73.0**	**21.9**	**0.3**	**4.8**	**0.766**	**65.8**	**16.6**	**14.0**
87 1)	25+27	240	110	260 (220.5)	90.5 (82)	450°	200	15.2	7.6	65.7	35.5	0	6.4	0.703	83.0	9.5	2.5
94 1)	**23+25**	**240**	**0**	**90** **(70.2)**	**24.5** **(15.8)**	**450°**	**200**	**0**	**0**	**51.5**	**37.8**	**4.0**	**6.7**	**0.777**	**71.9**	**11.3**	**13.1**
72	20	60	110	222.5	102	450°	*100*	12.9	12.9	87.5	20.8	0	4.6	—	36.3	18.4	43.5
68	27	60	110	220	92.5	450°	*300*	9.7	3.2	93.3	7.7		2.2	0.753	36.6	19.7	39.6

1) In these experiments the heating was interrupted half way through, the autoclave was cooled (pressures 82 and 15.8 kg. per sq. cm. respectively), hydrogen was added, in the case of experiment 87, to 110 kg. per sq. cm. (none was added in the case of experiment 94) and the heating resumed. The maximum pressures then attained were 260 and 90 kg. per sq. cm. respectively; 220.5 and 70.2 kg. per sq. cm. had been reached in the first period of heating.

Product						Gas										Hydrogen fixed	
ation			Bromine value (addition)			Gas charged (litres)		Gas obtained (litres) 3)									
Per cent. by weight on wax charged																	
Gasoline + Loss	Kerosene	Residue	Liquid product	Gasoline	Kerosene	Hydrogen	Oxygen	Total	Heavy hydro-carbons	Oxygen	Carbonmonoxide	Hydrogen	Other hydro-carbons	Nitrogen	C-atoms (av.) in other hydro-carbons	In g.	Per cent. on wax charged
—	—	—	—	—	—	105.2	1.4	106.8	—	1.0	0.0	104.5	0.3	0.6	—	—	—
2.8	2.4	94.5	4.8	35.1	26.6	109.7	2.0	112.4	0	2.0	0.0	109.0	0.4	1.0	4.4	—	—
2.9	**2.9**	**93.6**	**7.5**	**59.2**	**41.0**	**0**	**0**	**1**	**0.1**	**0.0**	**0.0**	**0.2**	**0.2**	**0.4**	**2.4**	—	—
9.7	8.3	80.5	8.2	30.0	16.9	106.9	2.0	104.6	0	0.2	0.4	101.4	1.8	0.8	3.0	0.5	0.3
15.9	**11.8**	**69.1**	**19.6**	**57.4**	**26.0**	**0**	**0**	**3.2**	**0.6**	**.0**	**0.0**	**0.3**	**1.3**	**0.8**	**2.3**	—	—
20.3	13.5	60.7	12.8	25.0	13.1	109.4	2.0	104.4	0	0.4	0.4	98.8	3.1	1.7	3.0	0.9	0.5
28.6	**15.1**	**48.8**	**25.1**	**47.6**	**20.8**	**0**	**0**	**5.8**	**1.3**	**0.0**	**0.1**	**0.7**	3.9	**0.7**	**2.2**	—	—
31.3	17.0	46.0	10.5	23.5	12.3	110.1	2.0	96.5	0.2	0.8	0.1	88.4	3.5	3.5	2.5	1.9	1.0
38.2	**16.5**	**35.2**	**27.5**	**44.3**	**18.5**	**0**	**0**	**10.4**	**2.4**	**0.1**	**0.1**	**1.0**	**5.7**	**1.0**	**2.2**	—	—
45.4	17.6	26.5	13.8	19.7	9.9	113.0	1.0	100.0	0.6	0.8	0.0	87.7	9.1	1.8	2.2	2.3	1.2
41.8	17.7	30.0	12.8	19.2	9.8	112.1	1.0	98.5	0.8	0.4	0.6	87.0	8.4	1.5	2.2	2.2	1.1
45.0	**17.4**	**25.3**	(27.4) 2)	**39.4**	**16.8**	**0**	**0**	**18.9**	**3.5**	**0.2**	**0.2**	**1.9**	**12.5**	**0.6**	**2.1**	—	—
56.6	13.7	7.8	12.8	15.3	7.6	113.8	1.0	101.0	1.0	0.4	0.7	77.0	20.4	1.5	2.5	3.3	1.6
56.7	13.0	7.3	15.0	17.4	8.3	113.0	1.0	100.5	1.3	0.6	0.5	75.3	21.2	1.6	2.4	3.4	1.7
50.6	**12.1**	**10.2**	(23.0) 2)	**27.7**	**11.7**	**0**	**0**	**32.5**	**4.3**	**0.5**	**0.4**	**2.3**	**23.7**	**1.3**	**2.2**	—	—
57.8	6.2	1.6	8.8	9.5	5.2	142.0	1.7	116.4	1.4	0.9	0.8	76.2	35.4	1.7	2.5	5.9	2.9
38.9	**5.8**	**6.7**	(17.5) 2)	**20.5**	**10.3**	**0**	**0**	**55.6**	**3.2**	**0.4**	**0.4**	**3.4**	**47.8**	**0.4**	**2.1**	—	—
33.3	16.1	38.1	—	18.3	10.1	126.4	1.1	115.5	0.6	0.8	0.5	107.5	4.7	1.4	2.1	1.7	1.7
38.0	18.4	36.9	14.3	22.1	11.3	103.1	0.3	86.5	0.9	0.5	0.3	74.5	7.8	2.4	2.4	2.6	0.9

2) Approximate determinations.

3) CO_2 absent.

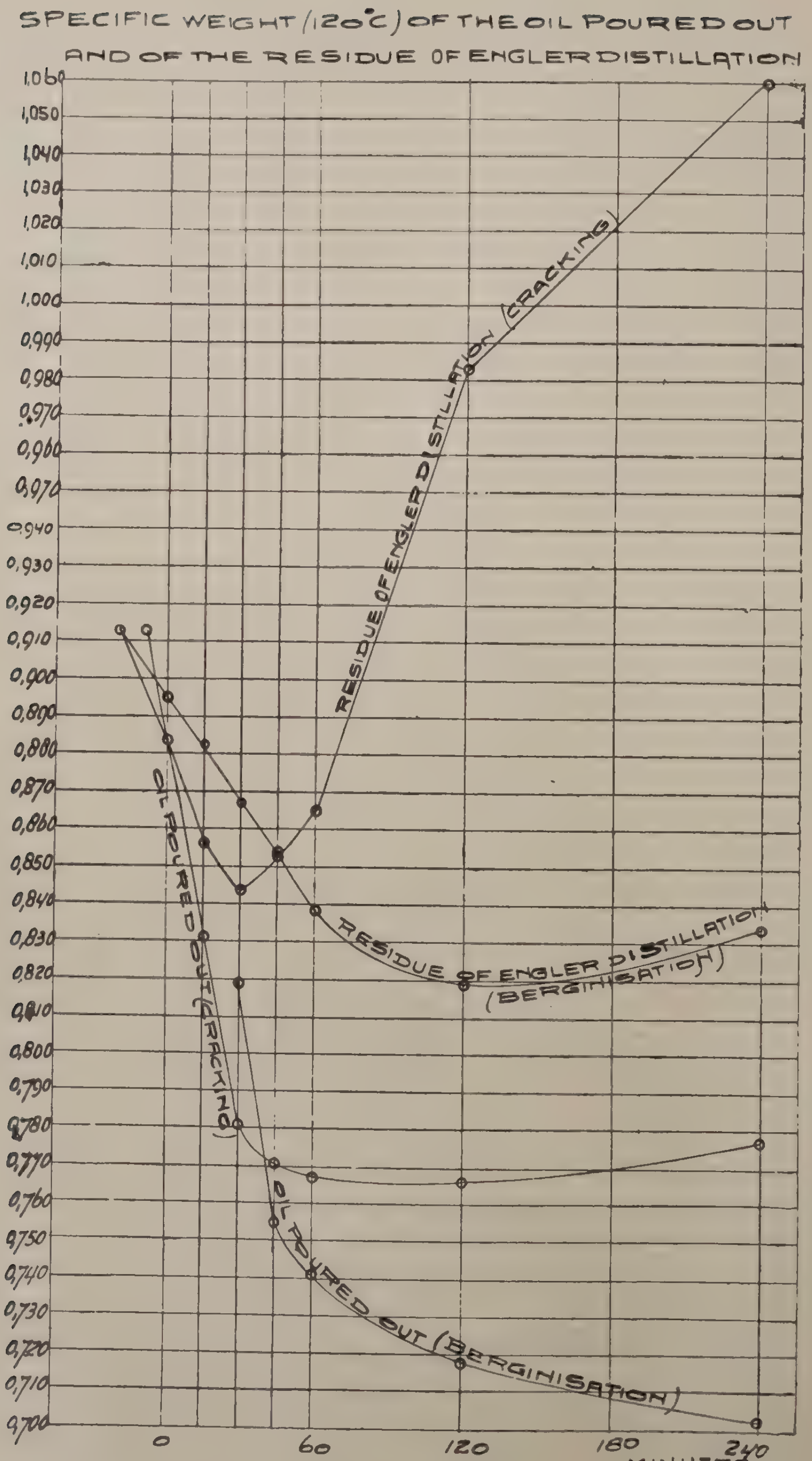

SPECIFIC WEIGHT (120°C) OF THE OIL POURED OUT
AND OF THE RESIDUE OF ENGLER DISTILLATION
1,060
1,050
1,040
1,030
1,020
1,010
1,000
0,990
0,980
0,970
0,960
0,970
0,940
0,930
0,920
0,910
0,900
0,890
0,880
0,870
0,860
0,850
0,840
0,830
0,820
0,810
0,800
0,790
0,780
0,770
0,760
0,750
0,740
0,730
0,720
0,710
0,700
0
60
120
180
240
MINUTES.
RESIDUE OF ENGLER DISTILLATION (CRACKING)
RESIDUE OF ENGLER DISTILLATION (BERGINISATION)
OIL POURED OUT (CRACKING)
OIL POURED OUT (BERGINISATION)

Fig. 4.

104, 102, 74, 76 and 80 after 15, 30, 45, 60, 60 and 120 minutes respectively, notwithstanding the decomposition which is taking place, give maximum pressures which are scarcely higher than those in experiments 99 and 106. This is doubtless because the effect of hydrogenation is becoming important. Confirmation is provided by the observed final pressures, which are smaller in proportion to the duration of the experiment. From the volume and composition of the gas obtained it follows that in experiments 103, 104, 102, 74, 76 and 80, and in 87 (where hydrogen was added twice), 0.3, 0.5, 1.0, 1.2, 1.1, 1.6 and 2.9 per cent. by weight of hydrogen respectively (calculated on the paraffin wax) are fixed. The bromine values of the original oil produced and of the corresponding gasoline and kerosene (Fig. 3) show that the bromine value is always lower than in the corresponding cracking experiments. A point of even greater importance is that after 60 and up to 120 minutes' Berginisation there is no decrease in the bromine value of the oil produced, as there is in the analogous cracking experiments. From this it may be concluded that probably polymerisation does not occur in these Berginisation experiments. It is only after further heating that the bromine value of the oil diminishes. Fig. 4 shows that after 120 minutes the specific gravity of the Engler distillation residue increases; up to 120 minutes' Berginisation this specific gravity diminishes.

The high hydrogen pressures used in Berginisation may be expected to modify the cracking process. A lower proportion of heavy hydrocarbons will be formed; in 99, 106, 103, 104, 102, 74, 76, 80 and 87, there are produced 0.0, 0.0, 0.0, 0.0, 0.2, 0.6, 0.8, 1.0 and 1.4 L. respectively. The longer the experiment lasts, the larger this quantity. This holds for the methane hydrocarbons also. In the Berginisation process there is less decomposition, for the average number of atoms of carbon per molecule, although it continuously diminishes, always remains greater than in the corresponding cracking experiments.

The change in the yields of gas, gasoline, kerosene and residue (Fig. 2) is an interesting result of Berginisation. The whole process is characterized by the formation of gas and gasoline and at first of kerosene, at the expense of the residue. Later, the percentage of kerosene diminishes. In our experiments the percentage of gasoline increased continuously. It is an important point that finally the residue almost wholly disappeared, so that only gases, gasoline and kerosene were left. The origin of the gasoline must be looked for in the cracking which is taking place.

These observations show that Berginisation results in a modification of the cracking process, gas and gasoline being formed initially in smaller quantity and of a less unsaturated character than the corresponding products of cracking. The falling off in the bromine value of the oil produced after a certain period of heating, and the continuous decline in the bromine value of the gasoline and kerosene, observed even more clearly in cracking than in Berginisation, must be attributed to the rupture of double bonds, followed by polymerisation in the case of cracking and, it may be supposed, by hydrogenation of the portions of the molecule, so that polymerisation is prevented or modified, in the case of Berginisation. This must be in close connection with the fact that in our Berginisation experiments practically no carbon (coke) is formed. The breaking up of molecules must take place throughout Berginisation, as otherwise the increase in the yield of gasoline, which finally exceeds that in the corresponding cracking experiments, could not be explained.

The direct addition of hydrogen to unsaturated hydrocarbons already present is not probable, because no catalyst is added and because the temperature is so high that in many cases the tendency is towards a decomposition of the corresponding saturated hydrocarbon into hydrogen and the unsaturated hydrocarbon rather than towards a reaction in the reverse sense, although this decomposition will be modified by the presence of hydrogen under high pressure. We hope to deal with this subject in more detail at a later date.

The advantage of Berginisation as compared with cracking appears

Nature of the Product and of the Destillation Residue.

Experiment	Minutes heating after the reaction temperature has been reached	Product	Residue
106	1	S_{pw}	S_{pw}
107	**1**	**S_{pw}**	**S_{pw}**
103	15	S_{pw}	S_{pw}
108	**15**	**S_{pw}**	**S_{pw}**
104	30	S_{pw}	S_{pw}
109	**30**	**S_v**	**S_v**
102	45	S_{pw}	S_{pw}
111	**45**	**L (dark)**	**S_v**
74	60	S_{pw}	S_{pw}
89	**60**	**L (dark)**	**S_v**
80	120	L (clear)	S_{pw}
78	60 (temp. 460°)	L (clear)	S_{pw}
92	**120**	**L (dark)**	**L (dark)**
87	240	L (clear)	L (dark)
94	**240**	**L (dark)**	**L (dark)**

S_{pw} = solid, like paraffin wax.

S_v = consistency of vaseline.

L (dark) = liquid, dark.

L (clear) = liquid, clear.

distinctly from the elementary composition of the residue in the two processes. For instance, in experiment 87 the composition of the residue was 85.4 per cent. carbon and 13.8 per cent. hydrogen, in 94 91.8 per cent. of carbon and 8.2 per cent. of hydrogen, respectively ; in other words, Berginisation prevents loss of hydrogen from the residues. This is of considerable importance, the process of cracking always giving oils or residues which are poorer in hydrogen, because in the gases formed, H_2, CH_4, C_2H_6, etc., an excess of hydrogen is present. This loss of hydrogen to some extent takes place during Berginisation, but in this process the loss of hydrogen is supplied from outside. The advantage of Berginisation is, therefore, proved. It is true that the hydrogen introduced from the outside is later found wholly or partly in the gases, but this supply of hydrogen has prevented a too extensive removal of hydrogen from the hydrocarbons. The great influence of temperature is shown by a comparison of experiments 78 and 80. In experiment 78 the temperature was ten degrees higher, and the effect was that in half the time (60 minutes in 78 and 120 minutes in 80) nearly the same result was obtained. Analogous observations were made by Dr. A. E. DUNSTAN [1]). The ten degrees higher temperature has apparently doubled the velocity of the complex of reactions. This fact being mentioned it must be added that without a more detailed study of this subject there is not much matter for discussion on the theoretical significance of this observation. That the quantity of paraffin wax used has a great influence appears from experiments 72 and 68, in which the percentage of fixed hydrogen is quite different. It is necessary, therefore, always to work under completely comparable conditions.

Summary. Comparative experiments show that Berginisation has various advantages over heating in absence of hydrogen under high pressures (cracking). After some hours' Berginisation a larger percentage of gasoline and of kerosene is obtained, while less gas is produced. Coke has not been formed to any material extent. The liquid products of reaction are more saturated. The residue on distillation (boiling point exceeding 300° C.) after 4 hours' Berginisation is but small. On the other hand, it must be observed that in Berginisation less gasoline and correspondingly less gas is formed initially than in the corresponding cracking experiments. In Berginisation cracking is restricted and the very reactive residues produced by cracking are converted into hydrocarbons of the gasoline and kerosene distillates. Polymerisation and the formation of coke from the unsaturated residues is thus prevented or diminished. While cracking gives rise to residue poor in hydrogen, Berginisation prevents the loss of hydrogen from residues. In one Berginisation experiment a residue was obtained which gave 13.8 per cent. of hydrogen, whereas the raw material contained 14.8 per cent. In a corresponding cracking experiment the residue contained only 8.2 per cent. of hydrogen.

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[1]) Journ. Institution Petroleum technol. **10,** 728 (1924).

Berginisation must be considered as a combined cracking and hydrogenation process. The useful feature of cracking, the breaking down of hydrocarbon molecules, remains, but is made more regular, while the products are obtained in a more stable condition on account of the addition of hydrogen, so that extensive polymerisation and formation of coke are avoided. The main feature of Berginisation is, therefore, not the saturation of unsaturated hydrocarbons already present. In this respect it differs widely from the ordinary hydrogenation of vegetable or animal oils, which is conducted in the presence of catalysts.

This investigation clears up the scientific significance of the Bergius hydrogenation process.

In continuation of this research the isolation, as far as possible, of the chemical compounds formed will be attempted, while our results on the hydrogenation of coal by the Bergius method will be published shortly.

We wish to express our thanks to Mr. A. C. OUBORG, who assisted us during the course of these investigations.

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Microbiology. — A. J. KLUYVER and H. J. L. DONKER: *"The unity in the chemistry of the fermentative sugar dissimilation processes of microbes."* (Communicated by Prof. G. VAN ITERSON JR.).

(Communicated at the meeting of November 29, 1924).

§ 1. *Introduction.*

Elsewhere [1]) one of us has elucidated how in metabolism of microbes two processes may be distinguished: dissimilation and assimilation, which respectively meet the energetic and material needs of the organism. In the same place it is further pointed out how two types have to be distinguished in the mode of energy supply, namely, those where the energy is derived from an oxidation with the absorption of free oxygen and those where the energy is derived from chemical reactions, in which free oxygen plays no part. These types of dissimilation are distinguished as oxidative and fermentative.

The sugar dissimilation processes brought about by microbes are of theoretical as well as of great practical importance. When one tries to obtain a summary of these processes based on the relative data in literature, it appears to be very difficult. One obtains the impression that among sugar fermenting microbes an almost unending variety of manifestations of life is present.

On the one hand this finds its cause in the fact that most microbes are described absolutely without any mutual relation, that is to say, without taking into account the natural relationships amongst microbes.

On the other hand this is a consequence of an almost complete lack of insight by the majority of investigators into the chemistry of the processes just mentioned.

In this communication we shall endeavour to bring order into this chaos of phenomena.

§ 2. *The classification of all sugar fermenting microbes into a limited number of natural groups.*

In the first place we will look into the question, how far it is possible to collect together the organisms under consideration into a number of natural groups according to their relationship.

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[1]) A. J. KLUYVER, Chem. Weekblad Vol. 21, p. 66, (1924).

TABLE I. SUMMARY OF THE GROUPS OF SUGAR-FERMENTING MICROBES AND THEIR CHARACTERISTIC PROPERTIES.

GROUPS.	MOST IMPORTANT PRODUCTS OF THE FERMENTATIVE SUGAR DISSIMILATION.	REMAINING CHARACTERISTICS.	EXAMPLES BELONGING TO THE VARIOUS GROUPS.
I. Alcohol yeasts.	Alcohol, carbon dioxide.	General properties of the Ascomycetes and related Fungi imperfecti.	*Saccharomyces cerevisiae* (Meyen) etc.
II. True lactic acid bacteria.	Lactic acid alone or together with acetic acid, alcohol, glycerol and carbon dioxide.	Gram positive, catalase negative, ·lack cilia. Do not form spores. Unable to synthesise protein from simpler nitrogen compounds.	*Lactobacillus Delbrücki* (Leichmann), *Lactobacillus fermentum* (Beijerinck) *Streptococcus lacticus* (Kruse), *Streptococcus pyogenes* (Rosenbach), *Streptococcus mastitidis* (Guillebeau), *Bacillus manniticus* (Gayon et Dubourg), *Lactobacillus pentoaceticus* (Peterson et Fred), *Leuconostoc mesenterioides* (Van Tieghem) *Bacterium gracile* (Müller-Thurgau et Osterwalder) etc.
III. True propionic acid bacteria.	Propionic acid, lactic acid, acetic acid and carbon dioxide.	As II but generally branched forms.	*Bacterium acidi propionici* (Freudenreich et Orla-Jensen) etc.
IV. Coli bacteria in the widest sense. (*Aerobacter*, Beijerinck).	Lactic acid, acetic acid, alcohol, sometimes 2-3 butylene glycol, formic acid. If gas always hydrogen along with carbon dioxide.	Gram negative, catalase positive, rod form with peritrichic cilia. Form no spores.	*Bacillus coli commune* (Escherich), *Bacillus lactis aerogenes* (Escherich), *Bacterium aerogenes* (American investigators), *Bacillus typhi* (Eberth), *Bacillus cloacae* (Jordan), *Bacillus ethaceticus* (Frankland), *Bacillus pneumoniae* (Friedländer), *Bacterium herbicola* (Burri et Düggeli), *Micrococcus prodigiosus* (Cohn), *Bacterium levans* (Wolffin) etc.
V. *Proteus*-bacteria.	As IV.	As IV but more adapted to the fermentative dissimilation of the hydrolytic decompositon products of proteins.	*Bacillus proteus vulgaris*, (Hauser) etc.
VI. Facultative anaerobic sugar fermenting spore forming bacteria.	Besides acetic and alcohol either 2-3 butylene glycol or acetone, carbon dioxide and hydrogen.	Als IV but spore forming, generally granulose as reserve material.	*Clostridium polymyxa* (Prazmowski) = *Granulobacter polymyxa* (Beijerinck) = *Bac. polymyxa* (Beijerinck). *Bacillus macerans* (Schardinger), *Bacillus asterosporus* (A. Meyer), *Bacillus acetoethylicum* (Northrop and others) etc.
VII. True butyric acid and butyl alcohol bacteria.	Butyric acid, acetic acid, butyl alcohol, isopropyl alcohol, acetone; carbon-dioxide and hydrogen.	Obligate anaerobic. Catalase negative, form spores, rod with peritrichic cilia. Granulose as reserve material.	*Bacillus amylobacter* (Gruber), *Bacillus amylozyma* (Perdrix), „Beweglicher Buttersäurebazillus" (Graszberger und Schattenfroh) *Granulobacter saccharobutyricum* (Beijerinck), *Granulobacter butylicum* (Beijerinck), *Granulobacter pectinovorum* (Beijerinck), *Clostridium pastorianum* (Winogradsky), *Bacillus granulobacter pectinovorum* (Speakman) etc.
VIII. Butyric acid and butyl alcohol bacteria of the paraputrificus group.	Als VII.	As VII but more adapted to the fermentative dissimilation of the hydrol. decomposition prod. of proteins	*Bacillus sporogenes enteritidis* (Klein), *Bacillus bifermentans sporogenes* (Tissier et Martelly), *Bacillus paraputrificus* (Bienstock), „Unbeweglicher Buttersäurebazillus" (Graszberger and Schattenfroh), *Bacillus oedematis maligni* (Pasteur et Joubert), *Bacillus botulinus* (Van Ermenghem) etc.

The relationship of the species belonging to one natural group should manifest itself both in the more important morphological and in the more essential physiological properties. In this connection no or at least far too little notice has been taken of the physiological properties by former investigators and there is no doubt that this circumstance is to a large extent the cause of the general chaos still prevailing.

This consideration has been ably put forward as far back as 1909 by ORLA-JENSEN in his ,,Hauptlinien des natürlichen Bakteriensystems'' [1]). As this investigator mentions, in the classification of bacteria one must, to quote verbally, ,,mehr Gewicht auf die inneren Eigenschaften als auf die aüszere Form legen''.

Without doubt metabolism occupies an important place among these inner properties. The chemical changes essential for the maintenance of life are nothing but a reflection of the chemical configuration of the living protoplasm on the nutriments offered or in other words: similar metabolism is a consequence of similar constitution of the most characteristic part of the microbe cell: the living protoplasm.

ORLA-JENSEN has taken these considerations carefully into account when concepting his natural system of bacteria.

Apart from this, it may be stated that certain natural groups of bacteria, such as those of the true lactic acid bacteria (ORLA-JENSEN's ,,Lactic acid bacteria'') [2]), those of the colibacteria, in the widest sense (BEIJERINCK's genus *Aerobacter)* [3]), those of the butyric acid and butyl alcohol bacteria (BEIJERINCK's genus *Granulobacter)* [4]) have become centra in the natural system for many microbiologists.

The system, drawn up recently by a committee of the ,,Society of American Bacteriologists'' [5]) fully takes into account a number of physiological characteristics, but suffers from the evil that the valuation of the more or less essential of the various properties is only slightly successful. [6])

However one should not imagine that the possibility of classifying all microbes in a limited number of natural groups has become common property of all microbiologists.

As to microbes, which are able to bring about fermentative sugar dissimilation, we will only express the opinion that it is possible to collect practically all these organisms into eight natural groups.

These groups and their characteristic properties are united in table I.

With reference to table I, we wish to mention firstly, that we have given only a few examples in column four, yet we know of no sufficiently described sugar fermenting microbes, which cannot be classed in one of the groups given.

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[1]) S. ORLA-JENSEN, Centralbl. f. Bakteriol. IIe Abt. Bd. 22, p. 305, (1909).

[2]) S. ORLA-JENSEN, The Lactic Acid Bacteria, Copenhagen (1919).

[3]) M. W. BEIJERINCK, Centr. f. Bakteriol. IIe Abt. Bd. 6, p. 193, (1900).

[4]) M. W. BEIJERINCK, Verhandelingen Kon. Ak. van Wetenschappen, Amsterdam, 2nd section Part 1. N⁰. 10 (1893).

[5]) BERGEY's Manual of Determinative Bacteriology, Baltimore 1923.

[6]) Compare for example: S. ORLA-JENSEN, Journ. of Bact. Vol. 6, p. 263, (1921).

Considering this, it may be taken as certainly surprising, that the diversity of sugar fermentative microbes can be reduced to such a small number of groups, which are characterized by relatively so large a number of correlating properties. When directing attention to the products formed in the fermentative decomposition of sugars, at first sight unmistakably a certain connection appears between the nature of the most important products from a quantitative point of view, and the classification into groups on the remaining properties. For instance in table 1 one finds lactic acid mentioned among the dissimilation products only in groups II, III, IV and V, 2 : 3 butylene glycol exclusively in groups IV, V, VI, while butyric acid, butyl alcohol and acetone are products which are limited to groups VI, VII and VIII.

On the other hand we must mention that the sugar decomposition products, which are formed by different microbes of one group, in some cases show great differences both from qualitative and quantitative standpoints.

This might give cause to doubt the correctness of the view which we expressed above, that the relationship of microbes is also portrayed in their metabolism.

A closer study of the chemistry of the fermentative sugar dissimilation of different microbes will however show that the differences in dissimilation of microbes belonging to the same group are in no wise of an essential character.

§ 3. *General considerations on the chemistry of the fermentation processes.*

Ever since a beginning was made with the closer study of fermentation processes, attempts to obtain a better idea of the chemistry of these decompositions have been made.

At first one has tried to represent the change brought about by one definite organism in a single chemical equation. As an example we mention only the equation originally given by HARDEN [1]) for the fermentation of glucose by *B. coli:*

$$2\,C_6H_{12}O_6 + H_2O = 2\,C_3H_6O_3 + C_2H_4O_2 + C_2H_6O + 2\,CO_2 + 2\,H_2.$$

Such a simple equation however is not satisfying, for the simple reason that the quantities of the fermentation products often show variations as the results of modification in the external conditions.

This fact has led some investigators to a mode of explanation in which it is assumed that each of the fermentative products is formed by an independent reaction of the sugar. In those cases where carbon dioxide and hydrogen are produced during fermentation, it is of course easy to write down a simple equation, in which a definite fermentation product is derived from the sugar molecule [1]) with the liberation of both gases mentioned. On the other hand it is obvious to what untenable consequences such an opinion leads for those fermentation processes, in which no free hydrogen is formed. BAUMGÄRTEL f.i., in order to explain in this way the occurrence of such products as glycerol and mannitol respectively in lactic acid fermentation has recourse to equations like: [2])

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[1]) A. HARDEN, Journ. Chem. Soc. Vol, 79, p. 612, (1901).

$$\underset{\text{glucose}}{7\,C_6H_{12}O_6} + 6\,H_2O = \underset{\text{glycerol}}{12\,C_3H_8O_3} + 6\,CO_2$$

$$\underset{\text{laevulose}}{13\,C_6H_{12}O_6} + 6\,H_2O = \underset{\text{mannitol.}}{12\,C_6H_{14}O_6} + 6\,CO_2$$

Between these two extreme opinions stands the explanation according to which a number of more or less independent reactions occur in the fermentation process. According to this supposition the fermentation products will owe their origin, partly to equally and partly to differently directed transformations.

One of the few examples worked out, is found in the study of GREY [3]) on glucose fermentation by means of *B. coli.* In this case the formation of lactic acid was considered to be a distinctly separate process from the formation of the other products, which would be produced from the glucose molecule according to the equation :

$$C_6H_{12}O_6 + H_2O = 2\,CO_2 + 2\,H_2 + C_2H_5OH + CH_3COOH.$$

In an number of cases GREY was able to explain in a satisfactory way the results obtained, in others however he was not successful. This caused him to abandon his scheme [4]).

Although undoubtedly the last considered general idea on the chemistry of fermentation processes is correct, it must nevertheless be stated that its application so far has borne but little fruit.

§ 4. *The fermentative decomposition of sugar in the light of* NEUBERG'S *investigations.*

A new light has been thrown on the chemistry of the fermentative decomposition of sugar [5]) by the researches during the last 14 years of NEUBERG and his collaborators. Their first investigations carried out on alcoholic fermentation made it highly probable that the ethyl alcohol produced originated from intermediately formed acetaldehyde [1]).

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[1]) Examples of this may be found, among others, in A. KIROW, Untersuchungen zur Buttersäuregärung, Reference Centralbl. f. Bakt. IIe Abt. Bd. 31, p. 534, (1912).

[2]) T. BAUMGÄRTEL, Grundriss der theoretischen Bakteriologie, Berlin (1924).

[3]) E. C. GREY, Proc. Royal Soc. Ser. B., Vol. 87, p. 472, (1914).

[4]) E. C. GREY, ibid. Vol. 90, p. 92, (1919).

[5]) Compare the most recent summary in this domain ; A. HARDEN, Alcoholic fermentation, 3rd. Edition, London 1923, in which one may find an almost complete list of Neuberg's communications.

In later years followed a series of researches on the fermentative decomposition of sugar under the influence of various bacteria, from which it appeared, that in all probability in these cases acetaldehyde also occurred as an intermediate product. By letting the fermentation take place in the presence of sodium or calcium sulphite or of "dimedon", they succeeded in establishing the formation of acetaldehyde addition products of the above substances.

Apart from alcoholic fermentation they proved this to be the case, for the fermentation of sugar by *B. coli commune*, *B. lactis aerogenes*, *B. dysenteriae*, "Gasbrandbacillus", *Bac. butylicus* Fitz and *Bac. butyricus* Fitz [2]).

Later on PETERSON and FRED were able to prove in the same way the formation of acetaldehyde by a bacterium of the coli group, by *Bac. acetoethylicum* and by *Lactobacillus pentoaceticus* [3]).

There is no doubt that these observations, which are to a great extent due to the initiative and intelligence of NEUBERG, are of fundamental significance for our insight into the fermentation processes. These researches have made it highly probable that the different fermentation processes of sugar primarily take the same course and that the observed variety in the final products are caused by differences in secondary transformations.

Yet it would appear to us that until now NEUBERG has not derived the full benefit of these important observations.

It is far from our mind to minimise the great significance of the fact that NEUBERG has succeeded in giving a detailed representation of the intermediate changes taking place in the alcoholic fermentation of sugar, which not only explains in an unconstrained way the occurrence of the normal fermentation products but also gives an explanation of the deviations in the course of fermentation in the presence of sulphites and of alkalies respectively (the so called 2nd and 3rd form of fermentation) [4]).

Still less do we overlook the fact that the observations made by NEUBERG on fermentations brought about by bacteria have given a securer basis to the hypotheses formulated by earlier workers on the origin of definite products in these fermentation processes. F.i. the demonstration of acetaldehyde as an intermediate product in the dissimilation of sugar has certainly given strong support to the idea already expressed by FITZ[1]) HARDEN[2]), GREY[3]), BUCHNER and MEISENHEIMER[4]) that this substance should be a link in the formation of such fermentation products as butylene glycol, butyric acid, butyl alcohol and ethyl alcohol.

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[1]) KOSTYTSCHEW was the first one who showed acetaldehyde to be an intermediate product in the alcoholic fermentation of sugars. See: Zeitschr. f. physiol. Chemie, Bd. 79, p. 130, (1912); ibid. Bd. 79, p. 359, (1912).

[2]) C. NEUBERG and F. F. NORD, Bioch. Zeitschr. Bd. 96, p. 133, (1919);
C. NEUBERG, F. F. NORD and E. WOLFF, ibid. Bd. 112, p. 144, (1920);
C. NEUBERG and B. ARINSTEIN, ibid. Bd. 117, p. 269, (1921).
H. KUMAGAWA, ibid. Bd. 131, p. 157, (1922). The honour is due to GREY for being the first to show in 1913 the occurrence of acetaldehyde in the fermentation of sugar by means of a bacterium (*B. coli*). Biochem. Journ. Vol. 7, p. 359, (1913).

[3]) W. H. PETERSON and E. B. FRED, Journ. of Biol. Chem., Vol. 44, p. 29, (1920).

[4]) Compare f.i. the summary of W. FUCHS, Der gegenwärtige Stand des Gärungsproblems, Stuttgart 1922.

It is equally acceptable, as NEUBERG postulated in the 3rd form of alcoholic fermentation, that acetic acid formed in bacterial fermentation owes its formation to a Cannizzaro transformation of acetaldehyde, especially when it is accompanied by at least an equivalent quantity of alcohol.

But all this does not remove the fact that NEUBERG has not yet succeeded in designing a complete scheme for any fermentation brought about by bacteria. Taking into consideration that with nearly all bacterial fermentations, certainly several, simultaneous independent reactions occur, one cannot require of such a scheme, that it will enable to predict the quantities of all the products formed in the fermentation. On the contrary, in designing a fermentation scheme one must take into consideration the fact, that as a consequence of different cultural conditions the various fermentation products likewise occur in varying quantities.

Yet such a scheme should enable to prophesy the consequences of the increase of one of the fermentation products on the quantities of the others.

In so far as, according to the scheme, the origin of two products is directly connected, one ought to find that an increase of one product goes parallel with a similar increase of the other product. Conversely, when certain products owe their origin to the same intermediate product, but are generated from it by independent reactions, one must observe that an increase of one product goes parallel with an equivalent decrease of other products.

A satisfactory scheme for fermentation should further fulfil the requirement, that with its help, one will be able to predict to a certain extent, the result of interfering in an artificial way with the equilibrium of the reactions.

§ 5. *General scheme for the fermentative decompositions of sugar, brought about by microbes.*

Supporting ourselves on the opinion expressed by NEUBERG, mentioned above, that primarily the same change lies at the basis of the different types of decomposition of sugar and especially under the strain of our conviction, that the relationship of microbe groups will express itself also in the kind of dissimilation reactions occurring, we have proceeded to draw up a scheme, which in our opinion, is able to give a picture of the whole domain of the fermentative decomposition of sugar and which fulfils in particular the above formulated requirements.

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[1]) A. FITZ, Ber. Bd. 13, p. 1309, (1880).

[2]) A. HARDEN and D. NORRIS, Proc. Royal Soc., Ser. B., Vol. 84, p. 492, (1912).

[3]) E. C. GREY, ibid. Vol. 87, p. 472, (1914).

[4]) E. BUCHNER and J. MEISENHEIMER, Ber. Bd. 41, p. 1410, (1908).

The scope of this study prohibits us, from entering into a detailed exposition of the arguments, which point in favour of the partial transformations, which lie at the basis of our scheme. It can only be pointed out that in the numerous former researches on one definite type of sugar fermentation experimental proofs are to be found to a large extent. We intend to give a detailed account elsewhere.

Our new scheme is given in Table II. (See Table following page).

Table II gives the reactions, which occur when the hexose molecule is decomposed by any fermentation process. Preparatory to discussing the reactions which are typical for the dissimilation of one particular microbe group in our scheme, a few remarks may be useful.

I. *The initial reaction.* We will state here, that we have fallen in with the hypothesis, as is assumed by previous investigators for some types of fermentation, that in all fermentative decompositions of sugar the hexose molecule is first converted into two molecules of an intermediate product of the empirical formula $C_3H_6O_3$. The course of this transformation and the composition of this intermediate products, which certainly is not lactic acid, will be left unconsidered here. We shall only express the opinion that in all fermentative decompositions of sugar the intermediate formation of hexose phosphoric acid esters certainly occurs, as has been shown by HARDEN and YOUNG for alcoholic fermentation [1]), by EMBDEN and LAQUER for the anaerobic decomposition of sugar in animal muscular tissue [2]) and very recently by VIRTANEN for sugar fermentation by true lactic acid bacteria [3]).

II. *The transformations of the hypothetical intermediate product.*

As appears from reaction equation IIa, we assume that the labile hypothetical intermediate product can change into the stable isomer : lactic acid. But simultaneously the intermediate product can undergo a second transformation (II*b*), in which it is broken up into formic acid and acetaldehyde. The possibility of showing formic acid and (intermediately) acetaldehyde in all fermentations brought about by bacteria, lends this reaction a high degree of probability, which is still further strengthened by a closer consideration of the metabolism of *B. typhosum* [4]) and the "selected

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[1]) See A. HARDEN, Alcoholic Fermentation, Chap. III.

[2]) See for example the summary by O. MEYERHOF, Die Naturwissenschaften, Bd. 12, p. 181, (1924).

[3]) A. I. VIRTANEN, Zeitschr. f. physiol. Chem., Bd. 138, p. 136, (1924).

[4]) A. HARDEN, Journ. Chem. Soc., Vol. 79, p. 612, (1901).

TABLE II. GENERAL SCHEME OF THE FERMENTATIVE SUGAR-DISSIMILATION PROCESSES OF MICROBES.

INITIAL REACTION:

I. $C_6H_{12}O_6 \rightarrow 2\ C_3H_6O_3$ (hypothetical intermediate product).

TRANSFORMATIONS OF THE HYPOTHETICAL INTERMEDIATE PRODUCT:

II*a*. $C_3H_6O_3 \rightarrow CH_3 . CHOH . COOH$ (lactic acid).
II*b*. $C_3H_6O_3 \rightarrow H . COOH$ (formic acid) $+\ CH_3 . CHO$ (acetaldehyde).

DEHYDROGENATION REACTIONS:

III*a*. $H . COOH +$ protoplasm $\rightarrow$ protoplasm hydride $+\ \overset{\nearrow}{CO_2}$.
III*b*. $CH_3 . CHO + H_2O +$ protoplasm $\rightarrow$ protoplasm hydride $+\ CH_3 . COOH$ (acetic acid).

CONDENSATION REACTIONS:

IV*a*. $2\ CH_3 . CHO \rightarrow CH_3 . CO . CHOH , CH_3$ (acetylmethylcarbinol).
IV*b*. $2\ CH_3 . CHO \rightarrow CH_3 . CHOH . CH_2 . CHO \rightarrow CH_3 . CH_2 . CH_2 . COOH$. (butyric acid).
IV*c*. $2\ CH_3 . COOH - H_2O \rightarrow CH_3 . CO . CH_2 . COOH \rightarrow \overset{\nearrow}{CO_2} + CH_3 . CO . CH_3$ (acetone).

PROTOPLASM REGENERATION REACTIONS:

V*a*. Protoplasm hydride $\rightarrow$ protoplasm $+\ \overset{\nearrow}{H_2}$.
V*b*. Protoplasm hydride $+$ acceptor $\rightarrow$ protoplasm $+$ reduced acceptor.

EXAMPLES OF THE PROTOPLASM REGENERATION REACTION:

V*b* 1. Protoplasm hydride $+\ C_3H_6O_3 \rightarrow$ protoplasm $+\ CH_2OH . CHOH . CH_2OH$ (glycerol).
V*b* 2. „ $+\ CH_3 . CHOH . COOH \rightarrow$ „ $+\ CH_3 . CH_2 . COOH$ (propionic acid).
V*b* 3. „ $+\ CH_3 . CHO \rightarrow$ „ $+\ CH_3 . CH_2OH$. (ethyl alcohol).
V*b* 4. „ $+\ CH_3 . CO . CHOH.CH_3 \rightarrow$ „ $+\ CH_3.CHOH.CHOH.CH_3$(2-3butyleneglycol).
V*b* 5. „ $+\ CH_3.CH_2.CH_2.COOH \rightarrow$ „ $+\ CH_3 . CH_2 . CH_2 . CH_2OH$ (butyl alcohol).
V*b* 6. „ $+\ CH_3 . CO . CH_3 \rightarrow$ „ $+\ CH_3 . CHOH . CH_3$ (isopropyl alcohol).
V*b* 7. „ $+\ C_6H_{12}O_6$ (fructose) $\rightarrow$ „ $+\ C_6H_{14}O_6$ (mannitol).

strains" of *B. coli* [1]) described by GREY. As regards alcoholic fermentation, it should be remarked that this mode of decomposition of the intermediate product $C_3H_6O_3$, put forward in 1906 by SCHADE [2]), is fairly generally abandoned at present for the change postulated by NEUBERG in which this substance should go over into pyruvic acid. Taking into consideration that pyruvic acid has not yet been demonstrated with certainty as an intermediate product in the fermentative decomposition of sugar, — we cannot accept the proof furnished for this view by VON GRAB[1]) nor that of FERNBACH and SCHOEN[2]), — we find as yet no reason to extend our scheme in this respect. Such an extension would only mean that in alcoholic fermentation the following reactions occur instead of reactions II*b* and III*a* :

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[1]) E. C. GREY, Proc. Royal Soc. Ser. B., Vol. 87, p. 472, (1914).
[2]) H. SCHADE, Zeitschr. f. physik. Chemie, Bd. 57, p. 1, (1906).

$$C_3H_6O_3 + \text{protoplasm} \rightarrow \text{protoplasm hydride} + CH_3COCOOH$$
$$CH_3COCOOH \rightarrow CH_3CHO + CO_2.$$

Since however, both ways lead to the formation of acetaldehyde, hydrogen combined with protoplasm and carbon dioxide[3]), the choice between the views is of subordinate importance[4]).

III. *Dehydrogenation reactions.* As a third type of reaction we have assumed that the protoplasm of the fermenting microbes has the property of oxidising various substances by removing hydrogen.

As is well known WIELAND has worked out a theory[5]) according to which the majority of all oxidations can be reduced to a removal of hydrogen from the oxidation substrate, either preceded or not by a preliminary hydratation. A powerful experimental support for this theory is undoubtedly the fact that WIELAND has succeeded in causing acetaldehyde to pass over into acetic acid and gaseous hydrogen in the presence of inorganic catalysts, (our reaction III*b)*[6]).

WIELAND has pointed out repeatedly the advantages which his assumption offers in the explanation of the chemistry of oxidative dissimilation processes. The possibility of extending his considerations to definite reactions in fermentative metabolism has been indicated here and there in his papers, but a thorough development of this idea, as far as we know, has not yet been given.

In our scheme we have limited ourselves to the insertion of two dehydrogenation reactions, namely of formic acid and acetaldehyde. Meanwhile it should be pointed out that the small quantities of succinic acid formed in some fermentations can at least partly owe their existence to the reaction which

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[1]) M. VON GRAB, Bioch. Zeitschr. Bd. 123, p. 69, (1921).

[2]) A. FERNBACH and M. SCHOEN, Comp. rend. T. 157, p. 1478, (1913); ibid. T. 158, p. 1719, (1914); ibid. T. 170, p. 764, (1920).

[3]) Cf. S. KOSTYTSCHEW, Die Pflanzenatmung, Berlin, 1924, p. 130.

[4]) A continuation of this study has caused us in the mean time to find extension desirable. We shall return to this elsewhere.

[5]) See: H. WIELAND, Ergebnisse der Physiologie, Bd. 20, p. 477, (1922); item Ber. Bd. 55, p. 3639, (1922) and also WIELAND's summary in OPPENHEIMER's „Handbuch der Biochemie" 2te Aufl., Jena, 1923 Bd. II, p. 252.

[6]) H. WIELAND, Ber. Bd. 46, p. 3327 (1913) and idem, Annalen der Chemie, Bd. 431, p. 301, (1923).

THUNBERG has made probable for oxidative metabolism in muscular tissue :

$$2\,CH_3COOH + \text{protoplasm} \rightarrow \text{protoplasm hydride} + \\ + COOHCH_2CH_2COOH$$

To the possibility of the hypothetical intermediate product undergoing dehydrogenation directly in alcoholic fermentation with the formation of pyruvic acid, we have referred above.

IV. *Condensation reactions.* As regards the reactions under this heading, we wish to remark that reaction IV*a* has been proved experimentally by the investigations of HARDEN [1]) and those of NEUBERG [2]). The second type of acetaldehyde condensation is also supported by experiment [3]). Reaction IV*c* is made sufficiently acceptable by the fact that production of acetone by suitable microbes is increased with practically the theoretical quantity by the addition of acetic acid during the fermentation process [4]).

V. *Protoplasm regeneration reactions.* The protoplasm hydrogen compound formed in the reactions described under III, is for different groups of microbes a more or less labile compound. If this compound is more labile it is able to decompose spontaneously into the original protoplasm and gaseous hydrogen (reaction V*a*). In the case of the more stable protoplasm hydride reformation of protoplasm is only possible by transferring the hydrogen to hydrogen acceptors present simultaneously (reaction V*b*). The presence of the ability of a definite kind of protoplasm to give rise to reaction V*a* nowise excludes reactions of type V*b* from taking place at the same time.

Reaction V*a* finds sufficient support in the occurrence of gaseous hydrogen in many fermentation processes. Reactions V*b*, which can occur in the normal dissimilation of sugar, become highly acceptable by the fact on the one hand, that all the products formed are met with among the end products of various decompositions of sugar and on the other hand by the circumstance, that exclusively those substances occur as acceptors, the presence of which in the fermenting medium, be it as substrate (laevulose) or as intermediate product, follows from the preceding reactions.

Meanwhile we wish to state definitely that other substances can also occur as hydrogen acceptors when these are present simultaneously. In this respect we refer to the "phytochemische Reduktionen" carried out by NEUBERG in alcoholic fermentation; which are in no wise limited to this type of fermentation.

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[1]) A. HARDEN and D. NORRIS, Proc. Royal Soc., Ser. B., Vol. 84, p. 492, (1912).

[2]) C. NEUBERG and E. REINFURTH, Bioch. Zeitschr. Bd. 143, p. 553, (1923).

[3]) See among several: C. NEUBERG, Bioch. Zeitschr. Bd. 43, p. 491, (1912).

[4]) REILLY and others, Bioch. Journal, Vol. 14, p. 229, (1920); see also: English Patent N⁰. 128403, (1919).

At this stage attention may be drawn to some points which can be deducted from our mode of consideration and which, in their turn are suited to demonstrate the correctness of our ideas regarding the course of fermentative dissimilation.

In the first place we wish to remark that our scheme fulfils the requirement, that it is possible to obtain an insight into the consequences, which arise from an increase in the quantity of one definite fermentation product on the quantities of the other fermentation products. It is obvious, that the prominent occurrence of reaction II*a*, i.e. the formation of lactic acid, must go parallel with a corresponding decrease of all changes, which are based on a IIb-reaction. A further consequence of the scheme which follows from reaction IIb is that the formic acid and the products formed from it (carbon dioxide and hydrogen) on the one hand and the acetaldehyde and the products formed from it by secondary reactions on the other, must occur in equivalent quantities, when all is calculated as grammolecules of the two mentioned starting products.

Our scheme contains further another specific requirement, which is also amenable to verification, i.e. that for the protoplasm hydride formation, an equivalent protoplasm regeneration must always take place. This includes that a quantity of hydrogen be it as gas or be it taken up by one or more of the acceptors (Vb-reaction), must be found which is equivalent to the quantity of carbon dioxide and acetic acid [1]) from equations IIIa and IIIb.

Making use of the quantitative results of fermentation found in literature and partly of fermentation balances determined experimentally by ourselves for various types of fermentative sugar dissimilation, it is now possible to test the correctness of the considerations given above. However, as this would lead us too far, we shall be satisfied here with the communication that, taking into consideration the great experimental difficulties, which are encountered in the quantitative determination of some fermentation products, the results obtained answer to the requirements of the scheme in a very satisfactory manner. We intend to elucidate this in more detail elsewhere.

But not only in this particular point do we see a confirmation of the correctness of our views. We will not neglect to emphasise here how the idea of WIELAND concerning the dehydrogenations and hydrogenations taking place under the influence of protoplasm, applied in this scheme, offers great advantages over the more general explanation of the phenomenon of oxidation and reduction processes occurring in the course of fermentation. Following NEUBERG's example these processes are fairly generally explained by the introduction of the well known Cannizzaro transformation.

Meanwhile it is in no way possible to explain with the aid of these transformations, which are always limited to aldehydes, the formation of a number of the products normally occurring in fermentations and obviously formed by reduction. We need only mention propionic acid, isopropyl alcohol, 2 : 3 butylene glycol, mannitol, etc.

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[1]) Taking into account also the separate formation of carbon dioxide and disappearance of acetic acid in those cases where acetone and (or) isopropyl alcohol occur as fermentation products.

Also the explanation of the occurrence of acetic acid in the fermentative decomposition of sugar, by means of a simple or mixed Cannizzaro transformation of acetaldehyde cannot in general be sustained, as in that case a quantity of monohydric or polyhydric alcohols equivalent to the acetic acid must always be formed. In the fermentation of sugar by true butyric acid bacteria considerable quantities of acetic acid are produced without alcohols occurring simultaneously. We proved the reduction-equivalent apparently missing to be free hydrogen [1]).

Not only does our scheme give an unconstrained explanation for all these facts but also it is excellently suited to throw a clear light on the unmistakable connection, which exists between the normal fermentation phenomena and the reducing powers of liquids in fermentation towards very diverse substances. In so far as the reduction of added aldehyde is concerned one can always keep to the explanation of a mixed Cannizzaro reaction of NEUBERG. But this explanation completely fails us in those cases, in which substances such as nitrobenzene, molybdenic acid, vanadic acid, methylene blue and sulphur are reduced. Everything is completely intelligible in the train of thought associated with our scheme since the substances mentioned simply act as hydrogen acceptors in reaction Vb.

On the basis of these facts it is evident that there exists no reason whatever to have recourse in certain cases to the narrower explanation afforded by a CANNIZZARO transformation.

The representation of the chemistry of the reduction and oxidation phenomena put forward gives at the same time means of explaining the connection, which undoubtedly exists between the chemistry of dissimilation and that of assimilation.

In this connection we will remind to the well known researches of FELIX EHRLICH on the primary reactions which α-amino-acids undergo in assimilation by alcohol yeast [2]). Nowadays the idea is fairly generally assumed that the first reaction of these α-amino-acids is an oxidation to the corresponding α-keto-acids with the splitting off of ammonia [3]). These in their turn are decomposed into carbon dioxide and the corresponding aldehydes, which are converted subsequently into the corresponding alcohols (the alcohols of fusel oil) by reduction and the corresponding acids by oxidation. The conversion of glutamic acid into succinic acid is the best known example of the latter change.

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[1]) An investigation of one of us not yet published (D.).

[2]) A list of EHRLICH's communications can be found in A. HARDEN, Alcoholic Fermentation, loc. cit.

[3]) O. NEUBAUER and K. FROMHERZ, Zeitschr. f. physiol. Chem. Bd. 70, p. 326, (1911); See also A. HARDEN, Alcoholic Fermentation, p. 137.

It is certainly important that these reactions completely fit into the spirit of the scheme. We need only add to this scheme a most obvious extension and assume that the protoplasm will exert its dehydrogenating action on the substrates of assimilatory metabolism and the primary oxidation of amino-acids to keto-acids appears as a self evident fact.

The reduction of the aldehydes to alcohols falls in completely with reactions Vb, just as was remarked above for the ,,phytochemische Reduktionen''. Finally, the sometimes continued oxidation of the aldehydes formed is completely comprehensible by the assumption of a further extension of the dehydrogenation reactions.

Still this is not all which can be put forward in favour of our views regarding the course of fermentation reactions.

Above we placed the requirement on a satisfactory scheme that by its aid one should be able to a certain degree to predict the result of artificial interference with the equilibrium of the reactions.

Owing to lack of space we shall not consider in particular, which predictions may be given for the various types of dissimilation on the basis of our scheme. We will be satisfied by stating that on the basis of many considerations taken from the scheme, we have come to the conclusion that by choosing suitable conditions it ought to be possible to bring about the fermentative production of acetyl-methyl-carbinol and 2 : 3 butylene glycol from *sugars* by means of yeast and representatives of the group of true lactic acid bacteria. As appears from our second paper, which immediately follows this, the results have completely confirmed our expectations.

§ 6. *The relationship of microbes expresses itself also in the fermentative decomposition of sugars.*

As already observed in the preceding paragraph we have considered for various microbes belonging to diverse groups in how far the observed results of fermentation answer to the requirements of the scheme put forward.

The limited available quantitative data naturally make it impossible to extend this investigation to all the kinds of sugar-fermentative microbes so far described.

But we can still see in how far the scheme is able to explain the qualitative results of all cases of the fermentative decomposition of sugar, which are sufficiently described, by the occurrence of a particular combination of partial reactions from the scheme. And the question naturally follows in how far the relationship of microbes from the same natural group expresses itself in the combinations of reactions to which their mode of fermentation may be reduced.

It suffices here to give in Table III, which combination of partial reactions is encountered with each of the species of microbes. We have limited

TABLE III. SUMMARY OF THE FERMENTATIVE DISSIMILATION OF SUGAR FOR THE VARIOUS GROUPS.

		GROUP I	GROUP II		GROUP III	GROUP IV			GROUP VI		GROUP VII	
		Alcohol yeasts	Homofermentative lactic acid bacteria	Heterofermentative lactic acid bacteria	True propionic acid bacteria	Sub-group of *B. typhosum*	Sub-group of *B. coli*	Sub-group of *B. aerogenes*	Sub-group of *Bac. polymyxa*	Sub-group of *Bac. macerans*	True butyl alcohol bacteria	True butyric acid bacteria
Initial reaction	I	+	+	+	+	+	+	+	+	+	+	+
Reactions of the hypothetical intermediate product	II*a* II*b*	− +	+ −	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +	+ +
Dehydrogenation reactions	III*a* III*b*	+ − ⊕	. .	+ +	+ +	− ⊕ +	+ ⊖ +	+ +	+ +	+ +	+ +	+ +
Condensation reactions	IV*a* IV*b* IV*c*	− ⊕ − ⊕ −	. . .	− ⊕ − −	− − −	− − −	− ⊕ − −	+ − −	+ + +	+ − +	+ + +	+ + −
Protoplasm regeneration reactions	V*a* V*b*	− +	. .	+ +	− +	− +	+ ⊖ +	+ +	+ +	+ +	+ +	+ − ⊕
Predominant protoplasm regeneration reactions	V*b* 1 V*b* 2 V*b* 3 V*b* 4 V*b* 5 V*b* 6 V*b* 7	+ . + ...	. . . .	+ . + . . . +	. + ...	. . + ...	. . + ...	. . + + . . .	. . + + . . .	. . + ...	. . . . + + .	. . . .

ourselves to one statement as far as these reactions are identical for various species of microbes belonging to one and the same group.

Groups V and VIII are not included in the table, because the types of sugar dissimilation of these groups are completely covered by those of groups IV and VII.

The table requires but little further explanation. We need only remark that the sign + indicates that for the particular microbes the corresponding reaction occurs in the normal fermentation of sugar; the sign — shows that the reaction does not take place; the sign ⊕ that a reaction not occurring under normal conditions can be realised under special conditions, while the sign ⊖ indicates that it is possible to cause a normally occurring reaction to disappear whilst retaining the remaining partial reactions.

Perusing this table, in the first place it may be taken as highly satisfactory that only a limited number of dissimilation types are encountered in each of the groups. Apart from any other consideration it need not be excluded that all the eleven differentiated types of dissimilation, should occur in each of the groups, which have been set up chiefly on the basis of other properties. In the fact that this is not the case we see a proof of our conviction expressed in § 2, that the relationship of microbes will be reflected in the kind of the dissimilation reactions. And this proof is still strengthened by a closer study of the different types of dissimilation met with in one and the same group, as it appears that the difference in one group can be practically always explained by the occurrence or non-occurrence of one single partial reaction, which then in certain cases carries with it the occurrence or absence of further secondary reactions.

For instance the difference between the homofermentative and heterofermentative lactic acid bacteria [1]) finds its explanation in the absence of reaction II*b* with the former.

The large agreement in the dissimilation reactions in the sub-group of *B. typhosum* and that of *B. coli* is obvious from the fact that GREY was able to obtain the so called "selected strains" by cultivating *B. coli* on media containing chloroacetates, the dissimilation of which strains was a picture of that of *B. typhosum*.

The difference between the subgroup of *B. coli* and that of *B. aerogenes* lies exclusively in the presence of the acetylmethylcarbinol condensation and the in consequence occurring prevalence of an other reduction reaction (V*b* 4) in the latter group.

The difference between the subgroup of *Bac. polymyxa* and that of *Bac. macerans*, according to the table is exclusively due to the presence of the IV*b* condensation in the former. Meanwhile this condensation occurs to such a small extent that it is justified to raise the question if there is sufficient reason for drawing up the subgroups. Nevertheless we decided to this differentiation because with the former the carbinol condensation and with the latter the acetylacetic acid condensation is so strongly pronounced.

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[1]) We introduce this nomenclature for the first time for describing the difference long known to the fermentation and dairy microbiologists between the true lactic acid bacteria which form exclusively lactic acid and those which also form volatile acids, alcohol and carbon dioxide.

Further, the difference between true butyric acid and true butyl alcohol bacteria may be ascribed to the fact that in the former the protoplasm hydride is more labile than in the latter, with the consequence that practically all hydrogen acceptor reactions remain absent.

Finally we will point out that for groups which from the data in the third column of Table I possess a closer relationship, this also holds true for the corresponding types of sugar dissimilation. Meanwhile we do not wish to conclude that similarity in type of sugar dissimilation, or more broadly : similarity in metabolism, always means a close relationship. It must never be lost sight of, that at one time or another in more or less independent phylogenetic series similar metabolism processes can occur.

Delft, November 1924.

Microbiology. — A. J. KLUYVER and H. J. L. DONKER : *"The formation of acetylmethylcarbinol and 2 : 3 butylene glycol in the fermentation of sugars by alcohol yeasts and true lactic acid bacteria."* (Communicated by Prof. G. VAN ITERSON JR.)

(Communicated at the meeting of November 29, 1924).

The formation of 2 : 3 butylene glycol and acetylmethylcarbinol in the fermentative decomposition of sugar under the influence of microbes was first demonstrated by HARDEN and WALPOLE in 1908 [1]). These investigators found that in the fermentation of sugar under the influence of *B. lactis aerogenes,* the glycol, together with small quantities of acetylmethylcarbinol, was present among the fermentation products to the extent of 20 percent of the weight of sugar fermented.

The mode of production of these two compounds was explained in 1912 by HARDEN and NORRIS [2]) by the assumption of a condensation of intermediately formed acetaldehyde.

In later years, a series of communications by LEMOIGNE [3]) has shown the occurrence of both the substances mentioned in the metabolism of very diverse microbes. Among these one finds both organisms, which possess exclusively an oxidative dissimilation and also those, which are able to bring about the splitting of sugars by fermentation. While we shall omit of consideration here the formation of acetylmethylcarbinol by the first mentioned organisms, we shall first consider to which of the groups given in the preceding communication [4]), the sugar fermenting microbes, which have been shown to produce these compounds, belong. It appears that all these microbes belong to groups IV and V. To this might be added immediately, that unpublished investigations, which we have carried out, have taught us that the products mentioned are also encountered very frequently among the normal fermentation products of microbes belonging to groups VI and VII. On the contrary these substances have not been found so far in the normal fermentative decomposition of sugar by microbes of groups I, II and III.

As will appear quite clearly from what is given below, this contrast is connected in a close manner with the fact, that free hydrogen is completely or almost completely absent among the fermentation products of the last mentioned groups of microbes.

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[1]) HARDEN and G. S. WALPOLE, Proc. Royal Soc. Ser. B. Vol. 77, p. 399, (1906).

[2]) A. HARDEN and D. NORRIS, Proc. Royal Soc. Ser. B. Vol. 84, p. 492, (1912).

[3]) M. LEMOIGNE, Annales de l'Institut Pasteur T. 27, p. 856, (1913); Comp. rend. de la Soc. de Biol. T. 82, p. 984, (1919); Ibid. T. 83, p. 336, (1920); Comp. rend. de l'Acad, d. Sc. T. 177, p. 652, (1923); Compt. rend. de la Soc. de Biol. T. 88, p. 467, (1923).

[4]) These Proceedings 28, p. 297 (1925).

A short time ago it was shown by NEUBERG and REINFÜRTH [1]), however, that if acetaldehyde is added to a sugar solution undergoing fermentation by brewer's yeast or pressed yeast, the acetaldehyde added is converted almost quantitatively into acetylmethylcarbinol. The fact that the product so formed appears to be optically active leaves no doubt as regards the biochemical character of the condensation which occurs. In this condensation NEUBERG sees a special case of the carbon coupling action of yeast, which he has established with a number of other aldehydes and which should take place under the influence of what he describes as a carboligase enzyme.

No further proof is necessary that this carboligatic action on added acetaldehyde is precisely the same as the condensation, which has already been recognised by HARDEN as the cause of the occurrence of acetylmethylcarbinol (and indirectly of 2 : 3 butylene glycol) in the normal fermentation of sugar by *B. lactis aerogenes.*

While on the one side, from the researches of NEUBERG and REINFÜRTH it appears that alcohol yeast is able to bring about the carbinol condensation of acetaldehyde and on the other side it is established that acetaldehyde is an intermediate product in the normal fermentation of sugar by this organism, the question naturally presents itself, why carbinol, or its reduction product 2 : 3 butylene glycol, is not formed in the normal fermentation, as has also been stated by NEUBERG.

The only plausible explanation for this fact is, that the acetaldehyde formed intermediately undergoes other transformations so rapidly, that it is withdrawn from the simultaneously possible carbinol condensation.

The scheme, which we have developed for alcoholic fermentation and which may be gathered from Tables II and III of our preceding communication, clearly indicates that it is the protoplasm-hydrogen compound, which makes itself master of the acetaldehyde. Indeed, where protoplasm regeneration with the liberating of free hydrogen by the yeast cannot take place, the re-formation of protoplasm is left completely to the collaboration of a hydrogen acceptor, the acetaldehyde then functioning as such.

If this view is correct, then interference with the metabolism, the direct consequence of which is the introduction at least partially of another protoplasm regeneration reaction, must result in an excess of acetaldehyde in first instance. Now where 'acetaldehyde added externally is converted by yeast into acetylmethylcarbinol, one might expect that the method of interference, described above, will lead in like manner to the production of the carbinol or to its reduction product 2 : 3 butylene glycol.

In this line of thought we have investigated the result of the addition of hydrogen acceptors on the course of the normal fermentation of sugar.

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[1]) Bioch. Zeitschr. Bd. 143, p. 553, (1923).

In complete agreement with expectation it appears, that if a ten percent glucose solution, to which 0.1 percent of methylene blue or a few percent of sulphur has been added, is allowed to ferment at a temperature of 30° C. by means of 10 percent pressed yeast (Koningsgist der Ned. Gist- en Spiritusfabriek, Delft) with the exclusion of air, the formation of 2 : 3 butylene glycol can be demonstrated with certainty in the completely fermented liquid within three hours. It is wellnigh superfluous to remark, that the added methylene blue was completely reduced to the leuco-compound, while in the other experiments the added sulphur was converted into hydrogen sulphide to a noticeable extent.

In these and all subsequent experiments the presence of acetylmethylcarbinol or 2 : 3 butylene glycol respectively, was demonstrated by the excellent method of LEMOIGNE [1]), in which first the carbinol present is converted into diacetyl by oxidation with ferric chloride and afterwards any glycol is oxidised by bromine [2]) in neutral solution to diacetyl also, the latter being indentified by steam distillation into an ammoniacal solution of nickel chloride and hydroxylamine, as the highly characteristic nickel dimethylglyoxime.

This confirmation of our expectations led us to the suggestion, that probably also with the heterofermentative, true lactic acid bacteria the absence of carbinol and glycol among the normal products of glucose fermentation — concerning which we especially reassured ourselves — must be ascribed neither to a lack of power to form carbinol. We found it to be possible to force the production of carbinol in sugar fermentation, in the same way as given above for alcoholic fermentation, for a couple of representatives of this groups, namely, *Lactobacillus fermentum* (BEIJERINCK) and *Betabacterium breve* (ORLA-JENSEN). As it is not possible to start with a large quantity of bacteria material, one must choose the added hydrogen acceptor for these bacteria in such a way, that there is no retarding influence on the growth. As appears from our scheme, laevulose is preeminently suitable for bacteria of the group mentioned, to serve both as dissimilation substratum and hydrogen acceptor. In a sterile culture liquid, consisting of yeast extract with 10 percent of laevulose, inoculated with one of the bacteria strains after incubating for several days (at 30°—35° C. for *L. fermentum* and at 25° C. for *B. breve,)* 2 : 3 butylene glycol could be demonstrated.

The positive results of these experiments opened up the possibility of investigating in this way whether, be it in a very small degree, laevulose also acts as a hydrogen acceptor in alcoholic fermentation.

As a matter of fact we found that 2 : 3 butylene glycol (together with some unchanged acetaldehyde) can be shown in the fermentation of a 10 percent solution of laevulose with 10 percent pressed yeast after three hours. Under the same conditions no glycol or carbinol and at most a trace of acetaldehyde appears to be formed in the glucose fermentation.

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[1]) M. LEMOIGNE, Annales de l'Institut Pasteur, T. 27, p. 856, (1913); Compt. rend. T. 170, p. 131, (1920).

[2]) To us it appeared that in this oxidation the presence of ferric chloride as a catalyst is necessary.

By fermenting 10 percent laevulose in LEBEDEW's maceration extract prepared from brewer's yeast, the hydrogen acceptor function of the laevulose according to the strong acetylmethylcarbinol reaction, becomes even more prominent, which is in every respect conceivable, on account of the direct contact of the laevulose in high concentration with the fermentative agent. By means of a special control experiment we convinced ourselves that by using glucose instead of laevulose no production of carbinol or glycol took place.

Thus we see how the general scheme for the fermentative decomposition of sugar, which we have put forward, has led to the fact, that in future the formation of acetylmethylcarbinol or 2 : 3 butylene glycol from laevulose under quite normal conditions of fermentation of this sugar by means of alcohol yeast must be taken into account.

Delft, November 1924.

Mathematics. — *"A Representation of the Linear Complex of Rays on the Points of Space"*. By Prof. JAN DE VRIES.

(Communicated at the meeting of January 31, 1925).

1. R. STURM (*Liniengeometrie*, I, p. 265) gives a simple derivation of the usual representation (1, 1) of the linear complex of rays $\mathbf{L}$ on space.

In order to arrive at *another representation* we assume a plane pencil (A, α) which does *not* belong to $\mathbf{L}$, and a point M outside it. The sheaf round the point A' chosen at random, is brought into a projective correspondence with the sheaf round A.

If R is the point of intersection of α with the ray r of the complex, ϱ the plane $A\,r$, ϱ' the plane through A' corresponding in the projectivity to ϱ, we consider the point of intersection R' of ϱ' and $M\,R$ as the *image* of the ray r.

Inversely an arbitrary point R' corresponds as *image* to a definite *complex-ray*. To the pencil of planes (ϱ') round $A'\,R'$ a pencil (ϱ') is associated. One of its planes passes through the point of intersection R of α and $M\,R'$, and its intersection with the null-plane of R is the ray r that is represented in R'.

2. *Singular rays* (*a*). Let N_0 be the null-point of α, r_0 a ray of the plane pencil (N_0, α). Any point R_0 of r_0 may be considered as the passage of r_0. If in the projective sheaves round A and A' the plane α' corresponds to α and if $r_0{}^\star$ is the projection of r_0 out of M on α', r_0 has for *image* the *point-range* on $r_0{}^\star$. The *plane pencil* (N_0, α) consists accordingly of rays which are *singular* for the representation. The *images* of its rays form the *plane pencil* $(N_0{}^\star, \alpha')$.

b. For a complex-ray r in the *null-plane* of A, R lies in A; any plane through r may be considered as a plane ϱ. The homologous pencil (ϱ') defines on $m \equiv M\,A$ a *point-range* which represents r.

This point-range is apparently the image of the *whole plane pencil* (r) round A; all the rays are *singular*. But also all the points of m are *singular* for the representation and each is an image of (r).

c. For the ray $A\,N_0$ R and ϱ are both indefinite so that it is represented by the *plane pencil* projecting it out of M. It is, therefore, a *cardinal ray* for the representation.

d. A ray r is also *singular* if $M\,R$ lies in ϱ'; in this case ϱ' contains the line $k' \equiv M\,A'$. The pencil (ϱ') round k' is projective with the pencil (ϱ) round the line k (passing through A).

The hyperboloid produced by them cuts α in a conic α^2 (through A). Through any point R of α^2 there passes a singular ray r (the intersection of ϱ with the null plane of R). Through a point P of k there pass two rays r resting on α^2; hence k is a *double directrix* of the scroll of the *singular* rays. As a plane through k contains one ray r, the scroll (r) is *cubical*; its other directrix is the polar line of k relative to **L**.

Each straight line of the scroll $(r)^3$ has for *image* the *point-range* (R') on a definite *generatrix* MR of the *quadratic cone* (M, α^2).

3. *Singular points* (*a*). If we choose R' in A', hence R in the point of intersection A_0 of α and MA', the rays r in the null plane of A_0 are projected out of A by a pencil (ϱ) round the axis $AA_0 \equiv a$; the homologous pencil (ϱ') round a' cuts MA_0 in A'. Accordingly A' is a *singular point* and the *image* of the *complex-plane pencil* round A_0.

b. A plane pencil of **L** which has its vertex on the ray $r_0 \equiv AN_0$, is represented by a point R', which is accordingly *singular*. If R describes the point-range on r_0, its null plane ϱ revolves round r_0 and ϱ' describes a pencil that is projective with the point-range (R), hence with the plane pencil (MR).

Consequently there is a conic σ^2 of which each point R' is the *image* of a *complex-plane pencil* containing r_0. These plane pencils form the *parabolic congruence* [1, 1] round r_0 as axis.

c. A complex-plane pencil (r) containing a ray of the plane pencil (N_0, α), is projected out of A by a pencil (ϱ) round the axis $AR \equiv a$. If R' lies on the homologous ray a', this point is *singular*, and the image of (r).

If $a^\star$ is the projection of a out of M on α', and $A^\star$ the projection of A, the singular point R' is the intersection of a' and $a^\star$. If a revolves round A, R' describes accordingly a *conic* $\sigma_\star{}^2$ which passes through A' an $A^\star$. Each of its points is the *image* of a *complex-plane pencil* which contains a ray through N_0.

Out of M $\sigma_\star{}^2$ is projected on α in a conic through the point A and the passage K' of k'. Through a' there passes a plane ϱ' which contains MR; hence R is a point of α^2 (§ 2) and α^2 is the projection of $\sigma_\star{}^2$.

d. M is a *cardinal point* of the representation. For if R' lies in M, R may be any point of α, ϱ' any plane through $k' \equiv A'M$, hence ϱ any plane through k. The complex-plane pencil in a plane ϱ is represented in M. M is apparently the *image* of the *net of rays* [1,1] in which **L** is cut by the axial complex round the axis k.

4. *Image of a plane pencil.* The rays r of a complex-plane pencil (N, ν) define on α a point-range (R) and a pencil of planes (ϱ) round AN. The corresponding pencil (ϱ') is projective with the plane pencil (MR). The *image* of the plane pencil is accordingly a *conic* ν^2 through M.

If N lies in α, all the rays except NN_0 have the same passage $R \equiv N$.

In this case the *image* consists of the *straight line* MN and the *straight line* through $N_0^\star$, that represents the ray N_0N.

In particular the plane pencil round A is represented by the line m and a line through $N_0^\star$.

5. *Image of a net of rays.* The rays of $\mathbf{L}$ resting on the line d, hence also on the polar line $d^\star$, form a $[1, 1]$. The rays resting moreover on k, have M for image; they form a quadratic scroll which cuts α in a conic $(R)^2$. The cone projecting it out of M, consists of straight lines which touch the image surface of the congruence at M. As each point R of α is the passage of a ray of the $[1, 1]$, each straight line MR contains one point R' outside M.

The image is accordingly a *nodal cubic surface* O^3 with a conical point in M.

O^3 contains the *conics* σ^2 and $\sigma_\star^2$, for each plane pencil that has a point of one of these curves as image, has one ray in the congruence. For the same reason the line m lies on O^3.

As d cuts three rays of the scroll $(r)^3$, there pass through M three straight lines of O^3, representing complex rays. O^3 also contains the point A' (image of a ray of the plane pencil round A_0), and a straight line through $N_0^\star$ (image of a ray through N_0).

6. *Image of a quadratic scroll.* The images of two nets of rays have in common the line m, the conics σ^2 and $\sigma_\star^2$, and besides a *twisted curve* ϱ^4 with node M. This is the *image* of the *scroll* $(r)^2$ which consists of the common rays of the nets.

We can also arrive at this image in the following way. The image curve of $(r)^2$ lies on the cone projecting the passage $(R)^2$ of $(r)^2$ out of M. Each generatrix contains one point R' besides M. Two rays r rest on k; hence M is node of the image curve, which is accordingly a ϱ^4.

7. *Scroll which is represented on a straight line.* The straight line $g^\star$ has three points in common with O^3 (§ 5); consequently there are three points R' which represent rays r that rest on d. The *scroll* (r) is *cubical* and has as directrix the projection g of $g^\star$ out of M on α. The polar line of g relative to $\mathbf{L}$ is apparently the second (double) directrix.

8. *Congruence which has a field of points as image.* The plane Ω of the field $[R']$ has two points in common with the image of a complex-plane pencil. Accordingly there exists a congruence $[2, 2]$ which has $[R']$ as image. This congruence contains the 5 plane pencils which are represented in the points of intersection of Ω with m, σ^2 and $\sigma_\star^2$.

Mathematics. — *"A Representation of the Quadratic Complex of Rays on the Points of Space"*. By Prof. JAN DE VRIES.

(Communicated at the meeting of January 31, 1925).

Representations (1, 1) of the quadratic complex of rays **Q** have been described by CAPORALI and by MONTESANO [1]. In the following paper a new representation is treated.

1. Let (A, α) be a plane pencil of **Q** with rays a, A' the center of a sheaf which is projective with the sheaf round the point A, and M a given point. If r is a complex ray, R its passage through α, ϱ the plane Ar, ϱ' the homologous plane through A', we consider the point of intersection R' of ϱ' and the line MR as the *image* of the ray r.

It appears in the following way that an arbitrary point R' is the image of a definite ray r. To the pencil of planes (ϱ') through the straight line $l' \equiv A'R'$ there corresponds a pencil (ϱ) through the homologous line l. Together with α the line MR' defines the point R; the plane Rl cuts the complex-cone $(R)^2$ of R along RA and along a second ray r, and this ray has R' for image.

2. Every ray a of (A, α), is *singular*, for any of its points may be considered as passage R. The plane ϱ corresponding to a point R must touch the cone $(R)^2$ along a. The point-range (R) is projective with the pencil of planes (ϱ), hence with the homologous pencil (ϱ'), and also with the plane pencil (MR). Consequently the locus of the points R' is a conic $\varrho_0{}^2$ through M which cuts the homologous line a'. If R gets into A, ϱ coincides with α, ϱ' with α', and R' gets into the point of intersection M^* of MA with α'. The *images* of the *singular rays* A are therefore *conics* through the points M and M^*.

Let α^* be the plane of the second complex-plane pencil that has A as vertex, a^* the intersection of α and α^*. Any plane through a^* may be considered as the tangent plane ϱ at A to the complex-cone (A, α^*). The image of a^* is accordingly the point-range on the line $m \equiv MA$.

The *image* of the *plane pencil* (A, α) is a *binodal cubic surface* $\mathbf{A}^3$ which has *conical points* in M and M^*.

If A^* is the vertex of the other complex-plane pencil in α, the tangent plane ϱ coincides with α for each point of the ray AA^*; in this case the image points R' lie on the line of intersection d of α' and the plane MAA^*.

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[1] Cf. R. STURM, *Liniengeometrie* III, 272 and 395. The representation of MONTESANO deals with a **Q** with two double rays.

3. The rays r^* of the *plane pencil* (A^*, α) are also *singular* for the representation. The plane ϱ coincides with α, R is an arbitrary point of r^*; hence R' is a point of the line of intersection of the planes α' and Mr^*.

The image of r^* is a *point-range*; the *plane pencil* (A^*, α) is represented on a *plane pencil* of α'.

Also the rays of the *plane pencil* (A, α^*) are *singular*, for R lies in A and ϱ is an arbitrary plane through r. The image of the ray r is the *point-range* on the line m.

If the line MR lies in the plane ϱ', the ray r is represented on the point-range of MR; it is, therefore, a *singular ray*. In this case ϱ' belongs to the pencil of planes through the line $k' \equiv A'M$, and ϱ to the pencil of planes through the homologous line k. The projective pencils (ϱ) and (ϱ') produce a hyperboloid; the *conic* α^2 along which it cuts the plane α, is the locus of R. Through each point of α^2 there passes a singular ray, s; it rests on k. A plane through k contains one ray s. Through a point of k there pass the four rays s of its complex-cone which rest on α^2.

There is accordingly a *scroll* $(s)^5$ of *singular rays* each of which has for *image* the *point-range* on one of the generatrices of the *cone* which projects α^2 out of M.

4. Any point R' of m is *singular* and the image of the plane pencil (A, α^*).

If R' lies in M, R is an arbitrary point of α, ϱ' an arbitrary plane through k', ϱ an arbitrary plane through k. Each complex-ray in ϱ has M for image. Hence M is a *cardinal point* of the representation and the image of all the rays of the congruence [2, 2] that rest on k.

5. There are two more groups of *singular points* R'; they were pointed out to me by Dr. G. SCHAAKE.

The complex-rays through a point R of α define a pencil of planes (ϱ) round the axis $a \equiv AR$. The homologous planes ϱ' round the axis a' (in α') generally define each a point R'. But if a' cuts the line MR, the point of intersection R' is the image of any ray r of $(R)^2$; hence it is *singular*. The plane pencil (A, α) is projected out of M on α' in the plane pencil round M^*; this is therefore projective with (A', α').

Consequently α' contains a *conic* σ^2 through A' and M^* of which all the points R' are *singular* and each is the *image* of a *complex-cone* that has its vertex in α.

The conic σ^2 is projected out of M on α in a conic passing through A_0 (passage of k') and A. Because a' cuts the line MR, there passes through a' a plane ϱ' which contains MR; accordingly R is a point of the *conic* α^2 and α^2 is the *central projection* of σ^2 out of M as center.

If R is a point of α^2, the tangent plane ϱ through $a \equiv RA$ to the complex-cone of R defines a plane ϱ' through a'; the image ϱ^2 of a contains, therefore, the point R' of σ^2. Consequently σ^2 is a curve of $\mathbf{A}^3$; together with d it forms the intersection with α'.

The *singular conic* σ^2 is the *image* of a *congruence* [4, 4] which has α^2 as *directrix*. For through a point X there pass the generatrices of the complex-cone of X which rest on α^2; a plane ξ contains two points of α^2, hence four rays r.

6. A ray a contains three singular points S of $\mathbf{Q}$ outside A. One of the plane pencils of S passes through α; all the rays of this plane pencil cut a in S and have the same plane ϱ. Accordingly the point of intersection S' of MS with ϱ' is *singular* and the image of the plane pencil.

The locus of S is the intersection of α with the singular surface Σ^4 of $\mathbf{Q}$, hence a curve σ^4 that has a node in the point where Σ^4 is touched by α. The planes ϱ envelop the tangent cone K_4 of the 4th class which has A as vertex; likewise the homologous planes ϱ' envelop a cone of the 4th class, K_4', with vertex A'. To each generatrix of the cone (M, σ^4) a tangent plane ϱ' of K_4 is associated and inversely. As M lies in four planes ϱ', the locus of S' has a quadruple point in M. A plane through M contains four more points S.

There is therefore a *singular twisted curve* σ^8 with *quadruple point* M of which each point represents a *plane pencil* which contains a ray of (A, a).

These plane pencils form together a *congruence* [4, 4]*. The curve σ^8 lies on $\mathbf{A}^3$, for each of its points is among others the image of a ray of (A, a).

7. The *complex-cone* of a point T cuts α along a conic τ^2. Any plane ϱ through $t \equiv AT$ contains two rays r_1, r_2, hence the homologous plane ϱ' through t' two points R'. To the plane Mt' there corresponds a plane ϱ which contains two generatrices of (T, τ^2) both of which are represented in M. A plane through M contains two more points R, hence two points R'.

The *image* of a *complex-cone* is accordingly a *twisted curve* τ^4 with *node* M. The curve τ^4 cuts σ^8 and σ^2 each in *four* points, for the cone (T, τ^2) contains four rays of the congruence [4, 4]* and four rays which cut α^2.

If T is a *point of* α, the image of its complex-cone consists of the point-range on MT, the point-range on a straight line of α' (image of TA^*), and a conic ϱ_0^2 (image of TA).

A *scroll* $(r)^2$ has also for image a *twisted curve* ϱ^4, which has a *node* in M.

If T is a *singular point* of $\mathbf{Q}$, the complex-cone has a double generatrix and consists of two plane pencils. The *image* of a *complex-plane pencil* is a *conic* ϱ^2 through M which cuts σ^2 and σ^8 each twice.

A *complex-conic* γ^2 is represented by a plane curve. The axial congruence [2,2] which has k for axis (§ 4), contains two tangents to γ^2; hence M is a node of the image curve. Each point R of the line of intersection of α with the plane γ of γ^2 corresponds to two rays r; accordingly MR contains two points R'. The points of intersection of γ and α^2 lie each on two rays r, which have the same point of σ^2 for image.

Consequently the *complex-rays* of a *plane* γ are represented by the points of a *plane curve* γ^4 which has M and two points of σ^2 as *nodes*. In four points it rests on σ^8, for four rays belong to the congruence [4,4]*.

If γ is a *singular plane* of **Q**, each of the plane pencils has a *conic* ϱ^2 as image. Two of the four points of intersection of these conics lie on σ^2, one in M; the fourth is the image of the common ray of the plane pencils.

8. The rays of **Q** which belong to a linear complex, form a congruence [2, 2]. Its image has two points R' outside M in common with a ray MR; they are the images of the rays through R. The rays of the [2, 2] that rest on k, form a scroll of the fourth order; its intersection with α consists of the ray a of the linear complex and a cubic. The generatrices of the cone that projects this curve out of M, touch the image surface at M.

Consequently the *congruence* [2, 2] is represented on a *surface* $\mathbf{B}^5$ with *triple point* M.

This surface has σ^2 as *nodal curve*, passes through MA and contains σ^8.

9. The rays of **Q** which cut two lines b and c, form a scroll $(r)^4$ with double directrices b and c. They are projected out of A by the tangent planes ϱ of a cone of the 4th class. Also the corresponding planes ϱ' form a system with index 4; hence M is a quadruple point of the image curve. The passages R of the rays r are projected out of M by a cone of the fourth order with two double generatrices. Accordingly the *image* of $(r)^4$ is a *twisted curve* ϱ^8 with *quadruple point* M which cuts each of the curves σ^2 and σ^8 eight times.

10. A point-range (R') on the line g' is the image of a scroll (r) which has the projection g of g' out of M as directrix. As g' contains five points of $\mathbf{B}^5$, there are five rays r which rest on b.

Hence g' is the *image* of a *scroll* $(r)^5$.

Three rays of (A, α) and one ray of (A^*, α) belong to $(r)^5$; they form with g the intersection with α.

11. A *field of points* $[R']$ is the image of a *congruence* [4, 4].

For the image of a complex-conic (complex-cone) contains four points R. The congruence has double rays in the lines of (A, α), contains the plane pencils $(A, \alpha^\star)$ and $(A^\star, \alpha)$ and also the scroll $(s)^5$ of the singular rays. It has two singular points of the second order on α^2 and eight singular points of the first order, which are at the same time singular points of **Q**.

12. The plane pencils of **Q** are represented in a double infinite system of conics ϱ^2 (§ 7). Through an arbitrary point R' there pass *four* conics, for the ray r that has R' as image, belongs to four plane pencils. If R' lies on the cone (M, α^2), each of these conics consists of the line MR' and a second straight line.

Through each point of σ^2 and σ^8 there pass ∞ curves ϱ^2; these points are, therefore, *singular* for the *congruence* $[\varrho^2]$; this congruence has M as *cardinal point*. Each plane through M contains *eight* conics; for its line of intersection with α carries *four* singular planes of **Q**. Any line C is therefore a chord of eight ϱ^2, and the ϱ^2 resting on l form a surface of the order 20.

Mathematics. — *"A Representation of the Rays of Space on a System of Conics"*. By Prof. JAN DE VRIES.

(Communicated at the meeting of January 31, 1925).

1. Through axial projection a twisted cubic ϱ^3 may be represented on a conic ϱ^2. The pencil of planes that has a straight line l as axis, defines on ϱ^3 the triples A_1, A_2, A_3 of an involution I^3. If B_k is the image of A_k, the triples B_1, B_2, B_3 on ϱ^2 also form an I^3. The tangents b_1, b_2, b_3 to ϱ^2 at B_1, B_2, B_3 define a triangle with angular points C_1, C_2, C_3; the locus of the points C_k is a conic λ^2 (*involutorial conic* of the I^3). We consider λ^2 as the *image* of the line l.

Let λ^2 be a conic circumscribed about a tangent-triangle $C_1C_2C_3$ of ϱ^2. To the points of C_k there correspond three points A_k of ϱ^3, which define a plane α. Through a point P of λ^2 there pass two tangents to ϱ^2; the points of λ^2 that are represented in the points of contact, define a chord p of ϱ^3. Analogously a chord q of ϱ^3 corresponds to a point Q of λ^2. The line l of α resting on p and q, is the axis of a pencil of planes, and defines therefore an I^3 on ϱ^3. The involutorial conic corresponding to this I^3, passes through the points C_1, C_2, C_3, P and Q; hence λ^2 is the *image* of l.

Through *four* points there pass *two* conics λ^2. For these points define four chords of ϱ^3 and these have two transversals l. To the involutions defined by them there correspond conics λ^2 which pass through the given points.

2. If l cuts the curve ϱ^3, I^3 consists of the pairs of an I^2, which are completed to triples by a fixed point. The conic λ^2 is in this case the combination of a tangent r to ϱ^2 and the involutorial line λ of an I^2.

The I^2 on ϱ^3 corresponds to an infinite number of secants l; these form the second scroll on the hyperboloid of the bisecants defined by I^2. The corresponding pairs of lines λ^2 have the involutorial straight line λ in common. The *complex of the secants* is accordingly represented on the ∞^3 *pairs of lines* each of which consists of a tangent r and a line λ.

The image of a bisecant of ϱ^3 is a pair of lines formed by two tangents r_1, r_2 of ϱ^2. The congruence $[1,3]$ of the *bisecants* is, therefore, represented on the ∞^2 *pairs* r_1, r_2.

3. If l describes a *plane pencil* (l), the corresponding involutions have in common the group in the plane of the pencil and the pair on the

bisecant through the vertex of the pencil. The *image-conics* λ^2 form a *pencil*; three of the base points lie in the angular points of a triangle circumscribed about λ^2. The *three pairs of lines* are the images of the three *secants* belonging to (l).

A *field of rays* $[l]$ has for image a *net* $[\lambda^2]$ with *three base points* (angular points of a triangle circumscribed about ϱ^2).

4. If a *net* of conics has *three arbitrary base points*, the curves λ^2 of the involution contained in it form the image of a *quadratic scroll* $(l)^2$. For the corresponding lines l must rest on three fixed chords of ϱ^3. The six secants belonging to $(l)^2$ have pairs of lines as images.

An *arbitrary scroll* $(l)^2$ is represented in a system $(\lambda^2)_2$ with *index two*. For on each chord of ϱ^3 there rest two lines l; hence two curves λ^2 pass through the pole of the image chord. There are six pairs of lines corresponding to the secants which cut ϱ^3 in its points of intersection with $(l)^2$.

A *sheaf* $[l]^*$ is represented in a *net* of conics λ^2 which pass through *one* fixed point, the pole of the chord corresponding to the bisecant through the vertex of the sheaf.

For through any two points there passes a λ^2; it is the image of the ray of the sheaf which cuts the two corresponding chords of ϱ^3.

5. On an arbitrary line l there rest four tangents to ϱ^3; two of the corresponding triangles circumscribed about ϱ^2 coincide in a point of intersection of λ^2 and ϱ^2.

If l lies in a *plane of osculation* ω of ϱ^3, two nodes of the I^3 defined by l coincide in the point of contact of ω; the conics λ^2 and ϱ^2 *touch* each other.

If l is the intersection of two planes of osculation, it is represented by a λ^2 which touches ϱ^2 twice.

The *congruence* [3,1] of the *axes of osculation* is accordingly represented in the system of the conics of the involution which *touch* ϱ^2 *twice*. Such a λ^2 is defined by its points of contact.

If l is an *osculating ray*, hence a secant lying in the plane of osculation of its point of intersection, one of the nodes of the I^2 lies in that point; the line λ of the involution passes through the point of contact of r.

The *congruence* [3,3] of the *osculating rays* is represented on the ∞^2 pairs of lines formed by a tangent of ϱ^2 and a straight line through the point of contact.

6. A *pencil* (λ^2) of which three base points define a triangle circumscribed about ϱ^2, contains three curves which touch ϱ^2. For the corresponding *plane pencil* (l) contains three rays that are intersections with planes of osculation through the vertex of the plane pencil. Besides (λ^2)

contains three pairs of lines touching ϱ^2 which belong to the secants of (l).

If the vertex of the pencil is the null-point of its plane, the three secants belonging to (l) are osculating rays and the base points of the pencil (λ^2) are the angular points of a triangle circumscribed about ϱ^2 besides the point of intersection of the lines which join the angular points to the points of contact of the opposite sides.

7. The image of a *congruence* [1,1] is an ∞^2 system of conics λ^2, two of which pass through any two points; they are the images of the rays resting on two chords of the ϱ^3.

A net $[\lambda^2]$ with *one* or *three* base points contains one λ^2 of the system; it is the image of the ray that passes through a given point or lies in a given plane (§ 4, § 3).

The plane pencils of the congruence are represented by pencils (λ^2) (§ 3). Their base points lie on the images of the two directrices, three on one of those conics, the fourth on the other conic.

To the [1, 1] there belongs a scroll $(l)^6$ formed by secants of the ϱ^3. The *lines of the involution* λ envelop a curve of the *fourth* class, for the rays which rest on a chord of ϱ^3, form an $(l)^2$ and this cuts ϱ^3 in four more points.

A *congruence* [1,1] that has *two chords* of the ϱ^3 as *directrices*, is represented in an ∞^2 system with *two base points*; two curves pass through any two points. The quadratic scroll of the secants belonging to the congruence, is represented in the pairs of lines consisting of the join of the base points and a tangent to ϱ^2.

8. On four chords of ϱ^3 there rest two transversals l. If the chords k_1, k_2, k_3 are given, we can choose a fourth chord k so that the two transversals coincide; in this case k must touch the hyperboloid with directrices k_1, k_2, k_3. Through a point R of ϱ^3 there pass four chords k; they are the common generatrices of the cone which projects ϱ^3 out of R and the cone of the tangents through R to the hyperboloid. Accordingly an arbitrary chord of ϱ^3 rests on the eight chords; the locus of k is, therefore, a *scroll* $(k)^8$ with *quadruple* curve ϱ^3.

In order to find the order of the image curve, we consider a straight line of the image plane. The polar lines of its points are the images of a scroll formed by chords of ϱ^3. This scroll has in common with $(k)^8$ the curve ϱ^3, which is to be counted four times; the rest of the intersection must consist of four chords. Hence the *scroll* $(k)^8$ is represented on a *curve* of the *fourth* order.

It is the curve which is enveloped by the conics of the involution with three base points. For these form (§ 1) a system with index two.

Mathematics. — *"A Representation of the Rays of Space on the Pairs of Points of a Plane"*. By Prof. JAN DE VRIES.

(Communicated at the meeting of February 28, 1925).

§ **1.** Let l be an arbitrary straight line which cuts the planes α' and α'' in the points L' and L''. L' and L'' are projected on the plane α out of the fixed points A' and A''; the projections L_1 and L_2 form a *pair of points* which we consider as the *image* of the *ray* l. Apparently two arbitrary points L_1 and L_2 of α generally define *one* ray.

Let G be a point of the intersection g of the planes α' and α''; all the rays of the sheaf round G are represented in the pair of points G_1, G_2, which we call a *cardinal pair*. The cardinal pairs form two projective point-ranges on the lines g_1 and g_2 (the projections of g out of A' and A''); these meet in the point of intersection G_{12} of g and α. Accordingly the point-ranges (G_1) and (G_2) lie *perspectively*; the *center of perspectivety* A_{12} is the point of intersection of α and the line a which joins the centers A' and A''.

Any two points of g may be considered as intersections with α' and α''. Hence any pair consisting of an arbitrary point G_1 and an arbitrary point G_2 may be considered as the image of the *cardinal ray* g.

If l lies in α', L' is an arbitrary point of $l' \equiv l$; if G_2 is the projection of the point $g\,l$, the image of l consists of G_2 and an arbitrary point L_1 of the line l_1 (the projection of l out of A' as center).

The rays in α' and α'' are, therefore, *singular rays*.

§ **2.** The image of a straight line d cutting a consists of two points D_1, D_2, that are collinear with A_{12}. The pairs of points on a line d_{12} through A_{12} are the images of the rays in a plane through a.

The pairs of points L_1, L_2 on an arbitrary line are the images of the rays of a bilinear congruence of which the directrices lie in α' and α''.

The *image* of a *field of rays* consists of the ∞^2 pairs of points L_1, L_2, of which L_1 lies on a straight line f_1, L_2 on a straight line f_2. One of these pairs is formed by the images G_1, G_2 of the plane pencil of the rays resting on g.

The point of intersection D_{12} of f_1 and f_2 is the image of a ray d which cuts a. The *congruence* of the rays for which the images L_1 and L_2 coincide, has accordingly one ray in any plane.

If D_{12} describes a straight line d_{12}, the points D' and D'' describe two projective point-ranges in α' and α'' and d envelops a conic which touches a. Hence through a given point there pass two rays d of the congruence in question; this has accordingly the symbol [2, 1]. In the plane (G_{12},a) the conic degenerates, for G_{12} is the image of a pencil in that plane.

Consequently *the rays with coinciding image points* are the *tangents* of a *quadratic cone* with *vertex* G_{12} which rest on the *fixed* tangent a [1].

§ **3**. *Image of a plane pencil.* The image of a plane pencil is formed by *two projective point-ranges* on two straight lines f_1, f_2. One pair consists of the image G_1, G_2 of the ray resting on g, and another pair, D_1, D_2, is the image of the ray that cuts a.

If we choose the line f_1 at random and if G_1 is its intersection with g_1,G_2 the point which forms a cardinal pair with G_1, f_2 must pass through G_2. If we associate two arbitrary points P_2, Q_2 of f_2 to two arbitrary points P_1, Q_1 of f_1, and if G_2 corresponds to G_1, the point-ranges on f_1 and f_2, which in this way have become projective, are the image of a plane pencil.

The projective point-ranges on f_1 and f_2 define a conic δ^2 as the envelope of the lines $l_{12} \equiv L_1 L_2$. One of the tangents through A_{12} contains the cardinal pair G_1, G_2, the other the pair D_1, D_2. If we consider δ^2 as the image of the plane pencil, the ∞^5 *plane pencils* of space are *represented* on the ∞^5 *conics* of a plane.

But in this way any conic is the *image* of *two* plane pencils; for each of the two tangents through A_{12} may be considered as $g_{12} \equiv G_1, G_2$, the other containing the pair D_1, D_2. The tangents through G_1 and G_2 define the carriers f_1, f_2 of the projective point-ranges.

By means of the conics δ^2 we find accordingly an *involution* in the *plane pencils of space.*

If the vertex T of a plane pencil lies in α', δ^2 degenerates. For in this case the image consists of the pairs formed by T_1 and the points L_2 of a straight line f_2 and of the pairs formed by the point G_2 on f_2 and the points L_1 of f_1.

If the whole plane pencil lies in α', each ray has ∞^1 images consisting of a point G_2 and a point of a definite ray of the plane pencil round T_1.

If the plane of the pencil passes through G_{12}, its image consists of two perspective point-ranges and δ^2 degenerates into two plane pencils. If the plane passes through a, the image consists of two collocal projective point-ranges.

§ **4**. *Image of a quadratic scroll.* The image is formed by *two projective point-ranges* on two *conics* $\alpha_1{}^2$ en $\alpha_2{}^2$. The points of intersection of $\alpha_1{}^2$ and g_1 form cardinal pairs with the points where $\alpha_2{}^2$ is cut by g_2;

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[1] A congruence [1,2] consists of the transversals of a conic and a fixed straight line cutting it. A [2,1] corresponds to it dually.

these pairs are the images of the rays that rest on g. The two rays resting on a have images L_1, L_2, for which l_{12} passes through A_{12}.

Let α_1^2 be an arbitrary conic, G_1 and G_1^* its points of intersection with g_1. If we pass a conic α_2^2 through G_2 and G_2^* and establish a projective correspondence between the point-ranges on α_1^2 and α_2^2 so that G_1 and G_1^* are associated to G_2 and G_2^*, we have obtained the image of a quadratic scroll. If the scroll has a *directrix* f' in α' and a *directrix* f'' in α'', its image is formed by two projective point-ranges on the lines f_1 and f_2. In this case the points $f_1 g_1$ and $f_2 g_2$ do not form a cardinal pair. To the image there belong also the pairs of points which represent the rays of the scroll in α' and α''.

§ **5.** *Image of a sheaf.* The rays through the point S make the fields of points $[L']$ and $[L'']$ perspective. Accordingly the image of the sheaf is formed by the pairs L_1, L_2 of *two projective fields.*

The plane pencil of the rays resting on g, has its image in the *cardinal pairs.* To the sheaf there belong two rays of the congruence [2, 1], the rays of which are represented by points D_{12}. These two points and the point G_{12} are the *coincidences* of the two fields.

If the projective correspondence between the points of the fields $[L_1]$ and $[L_2]$ is such that the cardinal pairs consist of homologous points, we have the image of a sheaf. In order to see this we investigate what this image, **B**, has in common with the image **V** of a field of rays and with the image **S** of an arbitrary sheaf.

The image **V** consists of the ∞^2 pairs L_1, L_2 on two lines f_1, f_2. The straight line f_2^* which is associated to f_1 in **B** cuts f_2 in the point G_2 which is associated to the point G_1 on f_1. Hence **V** and **B** have only this pair (G_1, G_2) in common. But a cardinal pair is the image of a sheaf (round G); accordingly the field of rays generally does not contain any ray of the congruence that has **B** as image.

Let L_1, L_2 be a pair of **B**, L_1^* the point which through **S** is associated to L_2. In this case the points L_1 and L_1^* are homologous in a projectivity that has all the points of g_1 as double points and is, therefore, a *homology*.

The center of the homology is a point L_1 to which **B** and **S** associate the same point L_2. But then **B** must be the image of a congruence [0,1], hence of a sheaf.

§ **6.** Let us suppose that a *homology* in α contains the cardinal points; these are the images of the rays of the congruence that is represented by the homology.

A ray of this congruence which cuts a, has for image a pair D_1, D_2. The line d_{12} through D_1 and D_2 contains also a cardinal pair and is, therefore, a double ray of the homology; accordingly this has A_{12} for center and its axis passes through G_{12}. The point-ranges on homologous

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lines are projective, hence images of a plane pencil that has a as a ray. Consequently the homology in question is the *image* of a *parabolic congruence* [1,1] that has a as *directrix*.

§ 7. *Image of a bilinear congruence*. The rays of a congruence [1,1] define a *quadratic correspondence* in α. For the line f' of α', which is the projection of a line f_1 in α, defines, together with the directrices r and s of the congruence, a quadratic scroll, hence a conic φ'' in α'', consequently also a conic φ_2 in α. The ray t' of the [1,1] that lies in α', defines a point G^* on g. Hence φ_2 passes through G_2^* and through the images R_2 and S_2 of r and s. These three points are the *cardinal points* of the latter system. The *cardinal points* of the former system are R_1, S_1 and the image G_1^* of the ray in α''.

The plane pencil of the congruence that has R' as vertex, has for image the point-range on $S_2G_2^*$, apart from the image of t'. Together with the point-range on R_1S_1 the cardinal point G_2^* forms the image of the ray t'.

The plane pencils of the [1,1] that have their vertices on s, are represented in the point-ranges on lines f_1 and f_2 of which f_1 passes through R_1 and f_2 through R_2; the plane pencil (f_1) is projective with the plane pencil (f_2). Analogously S_1 and S_2 are the centers of two projective plane pencils, and any two homologous rays contain the image of a plane pencil that has its vertex on the directrix r.

A *parabolic* [1,1] consists of ∞^1 plane pencils which have a ray r in common while the vertices form a point-range on r which is projective with the pencil of their planes. The quadratic scroll which has a line of α' as directrix, contains a ray of the plane pencil of the [1,1] that has R'' as vertex. The plane of this pencil touches the carrier of the scroll at R''; accordingly the conics φ'' have a fixed tangent at R''. But then the conics φ_2 have also the same tangent at R_2. Consequently the *quadratic correspondence* has *two coinciding cardinal points* in R_2; this is also the case in R_1. This result could be foreseen because in this case the directrix s coincides with r.

§ 8. We arrive at an *involution* in the *rays of space* by associating to a ray l with image L_1, L_2 the ray m of which the image consists of the points $M_1 \equiv L_2$ and $M_2 \equiv L_1$.

If l describes a plane pencil, L' and L'' describe projective point-ranges; hence L_1 and L_2 describe projective point-ranges on two lines l_1 and l_2. The points $G_1 \equiv g_1 l_1$ and $G_2 \equiv g_2 l_2$ form a cardinal pair. But this is not the case with the points $H_1 \equiv G_2$ and $H_2 \equiv G_1$; hence the point-ranges (M_1) on $m_1 \equiv l_2$ and (M_2) on $m_2 \equiv l_1$ form the representation of a quadratic scroll. Accordingly our *involution* transforms a plane pencil into a *quadratic scroll*.

The double rays of this involution form the congruence [2,1] found in § 2.

The rays in a plane through a are arranged in involutorial pairs.

To the ray g there corresponds the field of rays in the plane defined by $h_1 \equiv g_2$ and $h_2 \equiv g_1$.

§ **9**. As we pointed out, the conics δ^2 give rise to an *involution* in the *plane pencils of space*.

In this way each of the two systems of plane pencils of a congruence [1,1] is transformed in itself. Let us consider e.g. the pencils in the planes through the directrix r, which, therefore, have their vertices on the directrix s. Let δ^2 be the image of such a plane pencil; one of its tangents through A_{12}, G_{12}, contains a cardinal pair G_1, G_2, the other, d_{12}, contains the image (D_1, D_2) of the ray of the pencil that rests on a. The straight lines $f_1 \equiv R_1 G_1$ and $f_2 \equiv R_2 G_2$ carry the image points L_1, L_2 of the other rays of the pencil.

If we also draw the tangents f_1^* and f_2^* through R_1 and R_2, these contain the images of the rays of another plane pencil belonging to the system; now $d_{12} \equiv g_{12}^*$ contains the cardinal pair G_1^*, G_2^*, $g_{12} \equiv d_{12}^*$ the pair (D_1^*, D_2^*).

Any tangent l_{12} to δ^2 contains the image (L_1, L_2) of a ray of the former plane pencil and the image (L_1^*, L_2^*) of a ray belonging to the latter. The line l_{12} contains the images of the rays of a congruence [1,1] that has as directrices a straight line of α' and one of α''. This congruence has two lines in common with the given [1,1]; each of them belongs to one of the plane pencils in question.

An arbitrary line of α is, therefore, touched by one δ^2; accordingly the conics of our system form a *scroll*. The two conics meeting in A_{12}, are the images of the plane pencils lying in the double planes of the involution round r.

The *pairs of points* of the scroll are (S_1, G_2^*), (S_2^*, G_1) and the pair to which G_{12} belongs.

If the congruence [1,1] is *parabolic* with the directrix r, the conics of the system have the line $R_1 R_2$ as common tangent.

§ **10.** Let us now consider the system Σ of the *plane pencils* with *common ray* r that have their *vertex* in the point S (and which belong, therefore, to the sheaf round S).

All the conics δ^2 touch the straight line $r_{12} \equiv R_1 R_2$ and the intersection d_{12} of their planes and the plane (Sa); for each plane pencil has one ray in the latter plane and the images of these rays form two projective point-ranges on d_{12}.

Now to any plane pencil there corresponds the plane pencil of the rays that have their images on the tangents f_1^*, f_2^* through the points G_1^*, G_2^* on d_{12}^*. The new pencils form a congruence Σ^*; their planes pass through the point G^*. Evidently the plane pencils (f_1^*) and (f_2^*) are projective; hence the lines f' and f'' (in α' and α'') describe two projective plane pencils round $G^\star$ and the *planes* of the pencils of $\Sigma^\star$ envelop a *quadratic cone.* Consequently an arbitrary point lies on *two* rays of the pencils and an arbitrary plane contains *one* ray.

The system Σ is transformed by the involution into a *congruence* [2,1].

§ **11.** Let Σ be the system of the *pencils* in a *plane* ϱ that have one *ray* r in common. If the field of rays in ϱ is represented by the pairs of points on f_1 and f_2, the plane pencils of Σ have as images the conics which touch f_1, f_2, r_{12}, and g_{12}, which form accordingly a *scroll.*

Any line d_{12} defines one δ^2; the tangents $f_1{}^\star$ and $f_2{}^\star$ through the points $G_1{}^\star$ and $G_2{}^\star$ on d_{12} contain the images of the rays of the associated plane pencil. Any plane contains one ray of the system $\Sigma^\star$.

Let L_1 be a point of α, G_1 a point of g_1, δ^2 the conic which touches $L_1\,G_1$. The tangent d_{12} cuts g_1 in a point $G_1{}^\star$, which we associate to G_1. If we choose $G_1{}^\star$ arbitrarily on g_1, $A_{12}\,G_1{}^\star$ defines a δ^2 of which two tangents meet in L_1. Hence g_1 contains *three* points $G_1{}^\star$ for which $A_{12}\,G_1{}^\star$ and $L_1\,G_1{}^\star$ touch the same δ^2. Each of the three lines $f_1{}^\star \equiv L_1\,G_1{}^\star$ corresponds to a plane pencil of $\Sigma^\star$. Accordingly this system is a *congruence* [3,1].

It consists of the *pencils* in the *planes of osculation* of a *twisted cubic* of which the *vertices* lie on the intersection of two planes of osculation [1]).

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[1]) This congruence corresponds dually to the [1,3] which has a twisted cubic and one of its bisecants as directrices. The other [1,3] which consists of the bisecants of a curve ϱ^3, does not contain any plane pencils.

Mathematics. — "*Sur les correspondances planes symétriques* [2,2] *de la première classe, résultantes de couples de points conjugués par rapport à une conique*". (Lettre de Mr. E. VENERONI à Mr. JAN DE VRIES).

(Présenté par M. le Prof. JAN DE VRIES à la séance du 30me mai 1925).

Vous avez étudié, dans la Note „*Involutorial correspondences* [2,2] *of the first Class*" [1]) une remarquable correspondance plane symétrique [2,2] de la première classe, Γ, [2]) résultante des couples de points conjugués par rapport à une conique donnée, a^2, situés sur les coniques d'un faisceau (b^2).

Permettez que je Vous démontre comment on peut aussi l'obtenir, en particularisant quelques correspondances que j'avais déja rencontrées [3]) à savoir:

1. Les Γ possédant quatre points singuliers et quatre droites singulières, indépendantes, de la première éspèce [4]).

2. Les Γ qui sont douées de dix droites singulières de la première espèce, et qui, par conséquent résultent de couples de points conjugués par rapport à une conique [5]).

J'aurai, ainsi, l'occasion d'indiquer une construction de toutes les Γ résultantes de couples conjugués par rapport à une conique, aussi générale mais bien plus simple que celle que j'ai donné dans les notes mentionnées, qui est fondée sur les propriétés de la congruence [7,2] de droites et de sa surface focale.

Je veux bien ajouter, à mon tour, que la Γ engendrée par les couples de points conjugués par rapport à une cubique plane, signalée au § 3 de ma note *b*, avait été déja étudiée par Vous, dans votre Note „*On pairs of points which are associated with respect to a plane cubic*" [6]).

§ 1. On peut construire toute Γ possédant quatre droites singulières s_i et quatre points singuliers, B_i, indépendants, en rapportant projectivement le faisceau de coniques (b^2) ayant pour base les points B_i au faisceau tangentiel de coniques (β^2) ayant pour base les droites s_i, et en coupant chaque conique b^2 par les tangentes de la conique correspondante β^2 [4]).

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[1]) These Proceedings, Vol. **24**, 1921, p. 12—16.

[2]) On désignera avec Γ toute correspondance plane symétrique [2,2] de la première classe.

[3]) Dans mes notes:

a. Sulle corrispondenze piane simmetriche [2,2] della classe uno;

b. Principali tipi di corrispondenze piane simmetriche [2,2] della classe uno (Rendiconti del R. Istituto Lombardo di Scienze e Lettere, Milano. Vol. LI, 1918 pp. 374—387 et pp. 753—777.

[4]) Voir note *b*, § 2.

[5]) Voir note *b*, § 3, 4, 5.

[6]) These Proceedings, Vol. **12**, 1910, p. 711—715.

Parmi ces Γ se trouve la Vôtre, car les couples de points correspondants dans Votre Γ, situés sur chaque conique b^2 sont réunis par des droites qui enveloppent une conique β^2; et, comme la conique b^2 varie dans le faisceau, la conique correspondante β^2 varie dans un faisceau tangentiel, ayant pour base les quatre droites singulières que Vous avez indiquées par s_k.

Il n'est pas inutile de démontrer, réciproquement, quelle doit être la position rélative du quadrangle (B) et du quadrilatère (s) et comment on peut établir la projectivité entre (b^2), (β^2), pour obtenir Votre correspondance.

Il faut, d'abord, choisir (s), (B) de manière que deux côtés opposés quelconques de (B) soient tangentes à une même conique de (β^2), et déterminer, ensuite, la projectivité entre (b^2) et (β^2), en faisant correspondre à chacune des trois coniques de (b^2), qui se réduisent à deux côtés opposés de (B), la conique de (β^2) qui est tangente à ces deux côtés.

On peut obtenir le quadrangle (B) et le quadrilatère (s) de la manière suivante :

Ayant choisi, arbitrairement, le quadrangle (B), considérons une conique β_1, tangente à deux côtés opposés de (B), B_1B_2, B_3B_4, et fixons deux autres tangentes quelconques de β_1, s_1, s_2. Les s_1, s_2 et chacun des deux couples de droites B_1B_3, B_2B_4; B_1B_4, B_2B_3 déterminent deux faisceaux tangentiels de coniques; les couples de tangentes, qui, en dehors des s_1, s_2, sont communs à β_1 et aux coniques de chaque faisceau, sont conjugués en deux involutions entre les tangentes de β_1; les deux droites s_3, s_4 du couple commun aux deux involutions et les s_1, s_2, sont tangentes à une même conique β_2 avec les B_1B_3, B_2B_4, et à une même conique β_3 avec les B_1B_4, B_2B_3; c'est à dire qu'au faisceau tangentiel (β^2) de coniques, ayant pour base les quatre droites s_i, appartiennent les trois coniques β_1, β_2, β_3, tangentes respectivement, aux trois couples de côtés opposés du quadrangle (B).

§ 2. Cela posé, on rapporte projectivement le faisceau (b^2) au faisceau tangentiel (β^2), en faisant correspondre aux coniques dégénérées B_1B_2,B_3B_4; B_1B_3, B_2B_4; B_1B_4, B_2B_3 respectivement les coniques β_1, β_2, β_3.

En coupant chaque conique de (b^2) avec les tangentes de la conique homologue de (β^2), on obtient les couples d'une Γ, qui est la Vôtre.

Il suffira, en effet, de remarquer qu'on peut obtenir la courbe double de la Γ comme lieu des points de contact de chaque conique de (b^2) avec les tangentes de la conique homologue de (β^2): ce lieu sera, donc, lorsque (b^2), (β^2) sont arbitrairement choisis, une courbe du 8^me^ ordre; mais, dans le cas que nous examinons, les six droites B_i B_k se détachent de la courbe, et le lieu résiduel est une conique a^2; c'est donc la conique de BERTINI par rapport à chaque C_M^4 [7]); et, puisque les points où les tangentes en M à C_M^4 rencontrent de nouveau la C_M^4, sont les points homologues à M dans Γ, et se trouvent sur la droite polaire de M par rapport à a^2, tous les couples de Γ seront conjugués par rapport à la conique a^2.

§ 3. On en conclut aussi que Votre Γ est caractérisée, entre celles qui possèdent quatre points singuliers B_i et quatre droites singulières s_k, indépendants, par la propriété d'avoir de plus, comme droites singulières, les six côtés du quadrangle (B).

En effet, lorsqu'on engendre la Γ, comme au § 2, au moyen du faisceau (b^2) et du faisceau tangentiel (β^2), le lieu des points qui forment avec B_1 des couples de Γ, est une courbe du quatrième ordre, avec un point triple en B_1, que l'on peut obtenir en coupant chaque conique b^2 par les tangentes, issues de B_1, à la conique correspondante de (β^2); mais, si les droites $B_i\,B_k$ sont singulières, les trois droites $B_1\,B_2$, $B_1\,B_3$, $B_1\,B_4$ se détachent de la courbe; il faut donc qu'à la conique de (b^2), composée des deux droites $B_1\,B_2$, $B_3\,B_4$ soit homologue une conique de (β^2) tangente à la droite $B_1\,B_2$, et, de même, à la $B_3\,B_4$. On en conclut que la projectivité entre (b^2) et (β^2) fait correspondre à chacune des trois coniques dégénérées de (b^2), qui se réduisent à deux côtés opposés de (B), une conique de (β^2), qui est tangente à ces deux côtés.

La Γ, donc, est bien la Vôtre.

§ 4. Nous avons, tous les deux, remarqué, qu'une Γ, établie entre les points d'un plan, engendre aussi une [2,2] symétrique entre les droites du plan, Γ^*, qui est, pareillement, de la première classe; les Γ, Γ^* se déterminent reciproquement.

Or, des §§ 3, 5 de ma Note *b* on déduit que, étant données les Γ, Γ^*, associées entre elles, lorsqu'il y a dix droites (ou dix points) singuliers de la première espèce, la Γ (ou la Γ^*) résulte de couples de points (ou de droites) conjugués par rapport à une conique; proposition que l'on peut invertir, car pour ces dernières Γ (ou Γ^*) l'ordre de la courbe double (ou la classe de l'enveloppe double) est deux; il faut donc qu'existent dix droites (ou points) singuliers, supposés tous de la première espèce. [8])

Entre ces Γ se trouve la Vôtre, caracterisée par la propriété d'avoir, en dehors des dix droites singulières $B_i\,B_k$, s_k, les quatre points singuliers B_i.

§ 5. J'ai donné, pour une telle Γ, la construction suivante: Soit $\triangle$ une congruence de droites [7,2] de KUMMER, et soit π son plan singulier du 6me ordre. Faisons se correspondre sur π deux points lorsqu'ils sont les intersections avec π de deux droites de $\triangle$, telles qu'un plan focal de l'une et un de l'autre soient en faisceau avec π; deux droites qui soient les intersections avec π des plans focaux d'une même droite de $\triangle$.

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[7]) On désigne par C_M^4 la quartique lieu des couples de Γ situés sur les droites issues de M. Voir note *a* § 1.

[8]) Voir note *a*, § 6.

On obtient sur π deux correspondances Γ, Γ^*, associées entre elles: les traces sur π des dix plans singuliers du 3me ordre de $\triangle$ sont droites singulières pour Γ, dont les couples de points sont conjugués par rapport à la conique a^2, suivant laquelle le plan π touche la surface focale de $\triangle$ [9]).

§ 6. Voici comment on peut spécialiser cette construction pour obtenir Votre correspondance.

Soit F^4 une surface de STEINER; soient O son point triple, T le trièdre de ses droites doubles, Q le tétraèdre des plans qui la touchent suivant des coniques.

Sur un plan π, qui ne passe pas par O, les projections faites de O, des sommets de Q et les traces des faces de T sont les sommets B_i d'un quadrangle (B) et les côtés de son triangle diagonal t.

Alors il y a sur π une transformation quadratique Ω, dont t est le triangle fondamental et les sommets de (B) sont les points doubles.

On rapporte à chaque point M de F^4 le point M_1 de π, correspondant en Ω à la projection M_0 de M, faite de O sur π.

On obtient ainsi une réprésentation biunivoque bien connue ϱ, de F^4 sur π; les trois sommets de t sont l'image du point O, et les quatre sommets B_i de (B) sont les images des quatre points de F^4 alignés avec O et les sommets de Q.

Les droites telles que MM_1 forment alors une congruence [7,2], $\triangle$, dont π est le plan singulier du 6me ordre, tandis que six de ses plans singuliers du 3me ordre sont ceux qui projectent de O les côtés du quadrangle (B); en effet chacun d'eux, $B_i\,B_k$, — transformé en soi-même par Ω — est l'image de la conique de F^4 qui est dans le plan $O\,B_i\,B_k$; ce plan contient, donc, la courbe de la 3me classe, enveloppée par les droites de $\triangle$, qui unissent les points de la conique à leurs images sur la $B_i\,B_k$; il est, donc, un plan singulier du 3me ordre de $\triangle$.

Et alors, en construisant sur π les Γ, Γ^* de la manière exposée, six des dix droites singulières seront les $B_i\,B_k$, tandis que les quatre points B_i, par chacun desquels passent trois droites singulières, seront aussi singuliers; ce que précisément caractérise Votre correspondance.

§ 7. Voici, enfin, la construction de chaque Γ résultante de couples de points conjugués par rapport à une conique, que je désire de Vous signaler.

Etant données, dans le plan, la conique a^2, et une involution du 2me ordre et de la première classe, I^2, (il s'agira, dans le cas le plus général, d'une involution de GEISER, engendrée par un réseau de cubiques, avec sept points fondamentaux), il y a, sur chaque droite r du plan, un couple g de points conjugués par rapport à a^2 et séparés harmoniquement par le couple de I^2 situé sur la droite r. *Les couples g ainsi obtenus engendront la Γ.*

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[9]) Voir les § 3, 4, 5 de ma Note *b*, ou la construction se rapporte particulièrement au cas dualiste.

En effet, les couples de points de I^2 alignés avec un point M forment une cubique C^3_M, passant par M: la conique polaire de M par rapport à C^3_M et la droite polaire de M par rapport à a^2 se coupent en deux points; c'est à dire que chaque point du plan appartient à deux couples g, tandis qu'une droite quelconque contient un couple g. Les couples g engendrent donc une Γ.

On obtient tout de suite les dix droites singulières de Γ; en effet la transformée de la conique a^2 au moyen de I^2 est une courbe du 8me ordre, qui coupe a^2, en dehors des douze points qui sont aussi sur la courbe double de I^2, en dix couples de points de I^2; les dix droites qui unissent les deux points de chaque couple sont les dix droites singulières de Γ.

§ 8. La construction indiquée est valable pour toute Γ résultant de couples de points conjugués par rapport à une conique a^2; en effet, étant donnée une telle Γ, soit r une de ses droites singulières. Les couples de Γ situés sur les droites issues d'un point M de r engendrent une cubique C^3_M, passant par M; et les quatre points de contact de la cubique C^3_M avec ses tangentes issues de M sont sur a^2; tandis que M varie sur r, le groupe des quatre points varie sur a^2, et décrit une série g^1_4; on peut, donc, obtenir sur a^2 les groupes de cette série au moyen des coniques d'un faisceau (f), qui ne contient pas la conique a^2; le faisceau (f) sera projectivement rapporté aux points de la r, à chaque point M de r correspondra précisément la conique de (f) qui contient les quatre points de contact de la cubique C^3_M avec ses tangentes issues de M.

Or, si l'on coupe chaque conique de (f) par les droites issues du point correspondant M sur r, on obtient les couples d'une involution plane de la première classe I^2, dont les points fondamentaux sont les quatre points-base de (f) et les trois points de r qui appartiennent à la conique de (f) correspondante.

Le couple de I^2 et le couple de Γ, situés sur une même droite x se divisent harmoniquement; en effet la conique de (f), correspondant au point M commun aux droites r, x, contient les quatre points de contact de la cubique C^3_M avec ses tangentes issues de M; elle est donc coupée par chaque droite qui passe par M suivant un couple de points (de I^2) qui divise harmoniquement le couple déterminé par la même droite, en dehors de M, sur la C^3_M. On peut donc construire la Γ de la manière indiquée.

§ 9. Votre correspondance peut donc aussi s'obtenir au moyen de la même construction; il suffit de choisir, comme involution I^2, celle que l'on obtient en faisant correspondre entre eux deux points, lorsqu'ils sont les points de contact d'une droite du plan avec des coniques du faisceau (b^2); les sommets et les points diagonaux du quadrangle (B) seront, alors, les points fondamentaux de la I^2.

Botany. — *"The influence of temperature on protoplasmic streaming of Characeae".* By M. HILLE RIS LAMBERS. (Communicated by Prof. F. A. F. C. WENT.)

(Communicated at the meeting of February 28, 1925).

Although there is much literature about the influence of temperature on protoplasmic streaming in general — several researches dealing almost exclusively with the subject — yet the information nearly always proves to be qualitative. With regard to purely quantitative information on the contrary, one is almost entirely confined to the now rather old data of NÄGELI and VELTEN. Therefore it seemed desirable to study once more the influence of temperature, the more so because there is an apparent difference between the results of these two investigators. A short statement of the outcome of former workers will be given here, followed by a preliminary communication of the method used in this research and some results obtained.

In 1860 NÄGELI [1]) published his experiments with *Nitella syncarpa*, dating from as early as 1849. Therein he only mentions the lengths of time used by particles of the protoplasm in covering a certain distance, at temperatures from 0° to 37° C. He states that no streaming was to be seen at 0° C. and that it stopped — and quite suddenly — when he got beyond 37° C.

VELTEN [2]) experimented with *Chara foetida* among other plants. He, too, merely mentions lengths of time, and from his observations drew quite wrong conclusions about the increasing of velocity, as NÄGELI did before. At 0° C. he found streaming extremely slow, at about 42° C. "Wärmestarre" followed.

If one converts those periods of time into velocities as SCHAEFER [3]) did, the difference between the temperature-velocity relation according to the data of NÄGELI and those of VELTEN, shows clearly.

By constructing a graph from the converted values of NÄGELI and the corresponding temperatures, we obtain an evidently logarithmical curve; from those of VELTEN an irregularly broken "straight" line, sharply turning down above 39° C.

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[1]) CARL NÄGELI. Ortsbewegungen der Pflanzenzellen und ihrer Theile. Beitr. zur wiss. Bot. Heft II 1860, p. 77.

[2]) W. VELTEN. Die Einwirkung der Temperatur auf die Protoplasmabewegung. Flora 59, 1876, p. 209.

[3]) K. L. SCHAEFER. Zur Lehre von der Reaktion des Protoplasmas auf thermische Reize. Flora 85, 1898, p. 135.

A "modern" work on protoplasmic streaming was written by EWART [1]), who made a close and profound study of the temperature problem in which he traced too the influence of the timefactor: In his chapter "The influence of temperature" he gives data of Chara foetida and Nitella syncarpa, but merely at temperatures upward from 20° C. and 25° C. respectively, the temperature intervals being rather large. By converting his figures for harmless temperatures, an almost linear relation between temperature and velocity of streaming was obtained. In the discussion of my own results, I shall return to this point.

It proved desirable to construct a new apparatus for this investigation; as neither those used by the before mentioned authors nor those described elsewhere in literature (see COHEN STUART [2])) seemed to answer the required purposes, which were:

Any temperature should be easily kept constant within narrow limits.

It should be possible to obtain a higher or lower temperature at any desired speed i.e., a few minutes should suffice.

The apparatus drawn and described proved to answer the requirements fairly well. Water from the tap, having streamed so long that a constant minimum temperature has been reached (in summer about 12.5° C., in winter about 10° C. in this laboratory) is carried under constant pressure through a tube immersed in boiling water. Now different constant temperatures may be obtained by regulating the quantity of water flowing through this tube [3]).

From cock *A* tap water of the minimum temperature flows via tube *B* into the vessel *C*, hanging about 3 M. above the work table. Into this vessel also opens a wide tube *D* and a tube *E* of about the same proportions as *B*. In a time-unit more water flows in from *A* than may flow out through *E*. So the water level in *C* rises, and finally the water streams away through *D* too. The water flowing through *E* is now under constant pressure. By raising or lowering *E* with a rope over pulley *M*, this pressure may be varied.

The water streaming through *E* passes a tap *F*, the opening of which may be adjusted by means of a micrometer screw — speed 1 mm. The screwhead is a disk with 100 divisions so that it is possible to vary the taphole 10, if need be, 5 μ. Via this tap a regulated quantity of water flows through the tube *G* running through vessel *H*, in which the water is kept boiling rapidly by means of two Bunsen gas burners. The water quantity amounts

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[1]) A. J. EWART. On the Physics and Physiology of Protoplasmic Streaming in Plants. Oxford 1903.

[2]) C. P. COHEN STUART. Ein Mikrothermostat zum Studium der Protoplasmaströmung. Rec. d. trav. bot. néerl. Vol. XIX, 1922 p. 139.

[3]) I am greatly indebted to Mr. P. A. DE BOUTER, mechanic at the Botanical Laboratory for the care and attention he gave to the finishing of the apparatus. Many difficulties were solved by his clear insight.

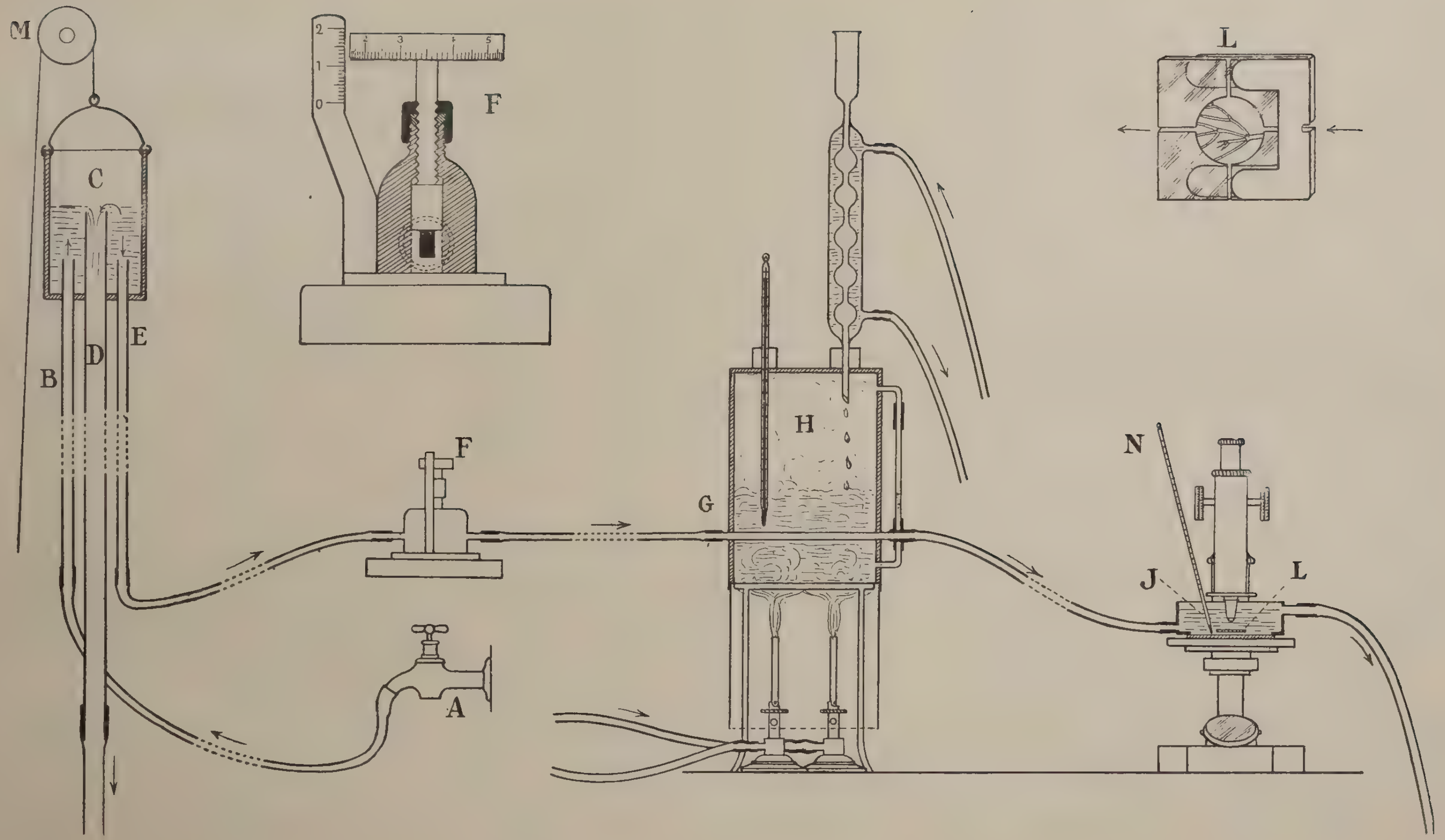

Fig. 1.

to a little more than $^1/_3$ of the volume of H. The original quantity is kept constant by an open condensation tube, fed by a fourth tube (not specified in the figure) coming from the vessel C. Except the bottom, H is totally isolated by a thick asbestos layer. A thermometer, gauge glass, and a screen around the gas burners need, perhaps, no further explanation.

Out of vessel C the now heated water flows into J, a somewhat boat-shaped little tank, that contains the object. In a vessel shaped in that manner there occurs no streaming of water of different temperatures, as has been proved.

Isolation was not necessary as the fall of temperature between entrance and exit proved to be extremely small, even at the highest temperatures. The object lies in a special objectroom made so that the water can pass through it, as has been demonstrated by filling the objectroom with Indian ink, which was quickly diluted and than disappeared entirely.

A section was removed from the metal bottom of J; under this a thick glass plate was attached. L lies about 3 mm higher on the remaining edge of the former bottom (not visible in longitudinal section).

The temperature of the object is measured by a very accurate quicksilver thermometer N divided into 0.1° C. The small bulb is placed as near as possible to the object. In order to protect the object, no strong objectives were used — always a carefully varnished objective III of LEITZ, combined with a compensation ocular 18 of ZEISS. In this way a quite efficient enlargement was obtained. The influence of the room temperature on the constancy of the temperature in J was particularly small. Direct sunlight has, however, been troublesome sometimes. In general, the temperature remained quite constant in the evening; therefore most observations were made then.

With this apparatus every desired temperature between about 15° C. (minimum temp. with widest opening of F) and about 55° C. may be obtained.

By tracing experimentally the temperatures corresponding to different positions of the screw and using a sufficient number of observations, one can construct the screw position-temperature curve, in order to interpolate from it the screw position for any desired temperature. This graph shows an asymptotic progress to both axes.

Temperatures under the minimum temperature of the tap water were obtained by siphoning ice water from a large tank containing broken ice. The velocity of streaming was regulated with a screw as F, the temperature of the water in J again quite depending upon the position of the screw. In this case the room temperature functioned as a practically constant heat source. In this way a temperature as low as 0.6° C. could be obtained.

Here, too, the different temperatures remained constant, because the room temperature, in absence of direct sunlight, varied very little or at any rate, very slowly.

The Characeae are still to be considered the standard material for all investigations on protoplasmic streaming. They may be cultivated rather easily during the whole year so one never needs to be without material. *Chara foetida A. Br., Nitella mucronata A Br. and Tolypella prolifera Leonh.* were used in this research. For the material of the last two species I am indebted to the kindness of Prof. Dr. J. C. SCHOUTE, who sent a large supply to me.

Nitella always proved the best object. Here the observation is not hindered by the development of cortex cells and the incrustation of Calcium carbonate, as is so often the case with the genus Chara.

In measuring, the usual method was followed. A net-ocular micrometer was put into ocular 18. With the enlargement used here, 10 divisions of the micrometer marked a distance of 555 μ. The time needed for a particle of the protoplasm to pass a distance of 10 divisions was measured. For each temperature 5 to 10 measurements were recorded, of which an average was taken. Time was measured by a stopwatch correct to 0.1 sec.

It would carry us too far to enter here into the many difficulties that may occur with such measurements. I will only draw the attention to a method of measuring yielding good results in cases in which the statistical method could not be used. In very young Characeae cells a regular rotating protoplasmic layer is seen, sometimes of a considerable thickness. All particles lying in that stream, big ones as well as small ones, are carried off with an equal velocity. Now it turned out that when a certain particle was followed, its rotation time had a constant value with constant temperature, besides being independent to its size. Especially at high temperatures at which the influence of the time factor was observed, this method was to be preferred to the usual one, each rotation being an expression of the velocity of the whole protoplasm.

Usually it was necessary to use a 100 candle lamp when making observ-

TABLE I

Februari 12th 1925. Whorlcell of Nitella mucronata A Br.

Temperature.	Time in 0.1 sec for 10 div. net-oc. Micr. = 555 μ.									
29.7° (1)	62	58	62	63	62	59	58	60	61	58
23.6° (2)	79	79	77	78	77					
21.3° (3)	88	87	86	85	85	86	85	85	83	85
19.1° (4)	97	97	99	97	95					
29.5° (5)	61	62	60	59	61					
32.3° (6)	54	52	53	53	54					
34.1° (7)	49	51	49	51	50					
22.1° (8)	83	85	80	81	82	82				

ations. No damaging effect of this light could be observed. The distance between the lamp and the mirror of the microscope was usually about 30 cm. The influence of radiating heat is certainly excluded by the streaming water. A young terminal shoot of Nitella, exposed to this lamp light 24 hours at a time, in an object room *L* [1]) showed acceleration of streaming but no injury whatever, in spite of the lamp being quite near the microscope.

In Table 1 the lengths of time of the first eight observations are given, the converted values of which may be found in the curve of Fig. 2.

In starting and stopping the watch a mistake amounting to 0.2 sec. for each measurement may be made, that is not easily taken into account.

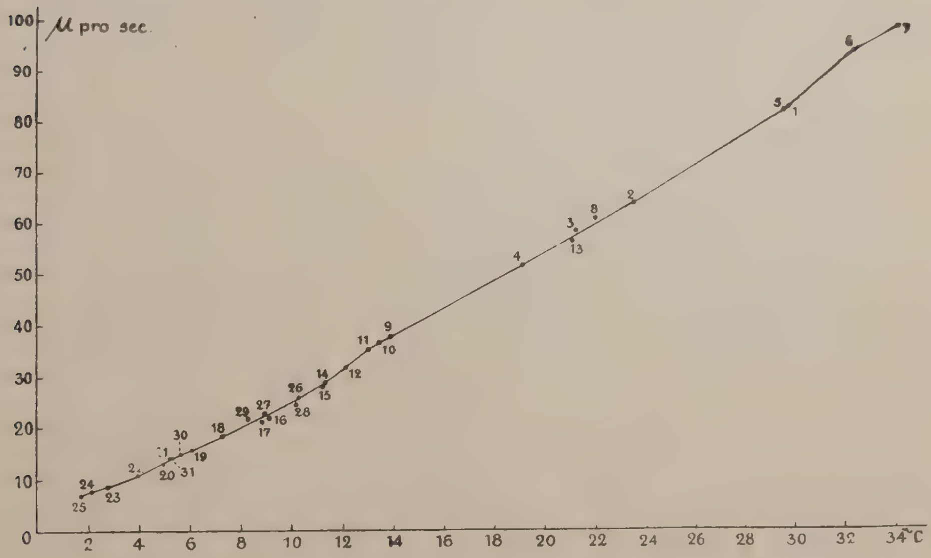

Fig. 2.

The curve in Fig. 2 refers to a whorlcell of *Nitella mucronata*. As in most experiments, here, too, the apical end of a young shoot was used. The numbers 1 to 31 at the dots of the curve, mark the order of the observations. One can see that the velocity data are reproducible, no difference of velocity being caused by the order in which the different temperatures act upon the object.

Sometimes the phenomenon of "shock" occurs when suddenly passing from a very high temperature to a very low one; streaming stops quite suddenly, and not until 10 to 20 min. afterwards is the velocity corresponding to the temperature attained. If no shock follows by changing the temperature, then the velocity of streaming adjusts itself always quite normally. The curve of Fig. 2 is typical for all Characeae I have observed until now. The conformity is so strong that Chara, Nitella and Tolypella at the same temperature often show velocities that are almost equal and sometimes are even quite the same. The curve often approaches a straight line, at least the part that contains the values above 14° C. By using short heating times (which is allowed with these objects under the mentioned circumstances, because another temperature and the corresponding velocity also, is almost immediately assumed) I could prove a few times that the temperature velocity curve continued its typical progress as far as 39° C. However, I have reason to believe that the velocity curve of the protoplasm itself will have slightly higher values than those got by measuring the particles carried off by the stream. Also the time factor may lower the velocities obtained above 30° C., a question into which I shall not now enter.

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[1]) *L* was placed on the stage of the microscope. Here the acceleration of streaming was an heat effect.

My own results, compared with those of NÄGELI and VELTEN, resemble for the greater part those of the later. How NÄGELI got a logarithmical curve so strongly bent is quite unintelligible to me. On the whole, the progress of this and other curves reminds one very strongly of fluidity graphs. (fluidity $= \frac{1}{\text{viscosity}}$).

EWART (p. 120 l.c.), too, states in his "summary of results", "As the temperature rises within certain limits the viscosity decreases, and a large part of the increased velocity of streaming is due to this cause alone".

I, no more than EWART, want to deny the existence of other factors, but I am convinced that the *visible* and *measurable* result of the influence of temperature is due to change of viscosity.

Botanical Laboratory.

Utrecht, February 1925.

Chemistry. — "*The Metastability of the Elements and Chemical Compounds as a Consequence of Enantiotropy or Monotropy*" IX.

By Prof. ERNST COHEN and Dr. A. L. TH. MOESVELD.

(Communicated at the meeting of November 29, 1924).

1. In a series of investigations, published[1]) under the above title with BRUINS, HELDERMAN, and KOOY, we have called attention to, and qualitatively and quantitatively proved, the fact, that the physical constants of the substances which have been determined up to this time, often refer to metastable mixtures of unknown composition of the modifications of those substances, so that no significance whatever can be attributed to those, quite fortuitous, values. Only then do they get any significance when those constants are determined for the pure modifications. In the case of cadmium iodide and ammonium nitrate respectively, we have already proved, that this may lead to errors of f.i. 5 and 9 %, but in certain cases much greater errors are also possible[2]).

In the course of this paper we wish to draw attention to two new cases which again indicate the absolute necessity of ascertaining that, in determining physical constants of solid substances, the pure modifications of the substance we wish to investigate are actually used, as otherwise absolutely valueless results are obtained.

The cases to be treated here refer to the determination of the specific heats of white (tetragonal), and grey tin, at temperatures lying between + 18° C. and the absolute zero, as well as the determination of the heat of transition of those modifications.

In the first place we point to the fact, that in our previous investigations[3]) we proved that these two modifications are enantiotropic, with the proviso, that grey tin is stable below the transition temperature of + 18° C., and white tin above this temperature. The phenomena of retardation in the transition of the white into the grey modification, however are so persistent, that down to very low temperatures the white tin can remain in a metastable state. It is owing to this fact that the phenomenon of stabilization at a low temperature (the transition from the white state into the grey, tin disease) has been discovered only in recent times.

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[1]) Zeitschr. f. physik. Chemie **94**, 450, 465, 471 (1920); **109**, 81, 97, 100, 109 (1924); **113**, 145 (1924).

[2]) The magnetic susceptibility of grey tin, according to the investigations by HONDA is different from that of white tin, not only in sign, but more than ten times as great. The presence of only a few per cent of one modification by the side of the other would, in this case, lead to very important errors.

[3]) Zeitschr. f. physik. Chemie **30**, 601 (1899); **33**, 57 (1900); **35**, 588 (1900); **48**, 243 (1904); **50**, 225 (1905); **53**, 625 (1908); **68**, 214 (1909).

2. It is true that in a previous paper we indicated, how it was possible to greatly accelerate stabilization, (adding germs of grey tin, as well as a solution of an electrolyte, at temperatures below the transition point, while at the same time we must take into consideration, that there is an optimum temperature for stabilization, *which depends on the previous history of the material*), by which means it has become possible to prepare unlimited quantities of grey tin in no long time (days, weeks), but we have been careful not to give the physical constants of grey tin, such as density, specific heat, heat of transition, etc. because our investigations in this direction, had never been made in such a way, that we were sure of having the absolutely pure grey modification. In agreement with this we wrote, after concluding this part of our investigations, in ABEGG's Handbuch der anorganischen Chemie 1):

"*Graues Zinn*. Das spez. Gewicht dieser Modifikation ist bisher nicht genau ermittelt worden; die Messungen von SCHERTEL, RAMMELSBERG, HJELT und STOCKMEIER beziehen sich alle auf Gemische von grauem und weissem Zinn, doch dürfte es in der Nähe von 5.8 bei 15° C. liegen". And further: "Dem von BUNSEN ermittelten Werte für die spezifische Wärme des grauen Zinns (er fand dafür 0.0545) kann eine Bedeutung nicht beigelegt werden, da das von ihm untersuchte Präparat offenbar ein Gemenge von weissem (tetragonalem) und grauem Zinn gewesen ist".

If it is not certain, that the material to be investigated is composed of a single, pure modification, the determination of physical constants is of course without any value whatever.

3. It is often difficult to prepare such a pure material, and this is especially the case with tin, where the retardations in the stabilization are so very persistent. Neither is it easy in such a case to find a sharp criterion which demonstrates that the transition in the desired modification has completely occurred. Consequently the proof will be found in this paper that up to the present the preparing of a preparation of grey tin, answering to the requirements that ought to be fulfilled, has not been successful.

4. During the last twelve years more than one investigator has tried to determine accurately the specific heats of the two modifications of tin

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2) Vol. **3**, (2) 556 (1909), Leipsic.

which we are discussing here: Wigand[1], Brönsted[2], and of late Lange[3] have occupied themselves with this problem.

We need not enter into the first investigation of Wigand[4], as he himself has withdrawn the results he then obtained.

But the second communication by Wigand is of no importance to us either, if we adopt the standpoint that we may only expect reliable results, if the *chemical* purity of the material used answers the necessary requirements. Now Wigand himself says however: "Eine Untersuchung der Präparate auf ihren Gehalt an reinem Zinn wurde unterlassen, da es im wesentlichen nur auf das Vorzeichen der Differenz der spezifischen Wärmen beider Modifikationen ankam".

5. Brönsted writes as follows about his material, used in determining the mean specific heats between 0 and 19°.00 C. and about the results he obtained:

1. *Weisses* (*tetragonales*) *Zinn*. Reinstes Metall von Kahlbaum bezogen:
0.05386; 0.05383; 0.05379; 0.05374; 0.05389, Mittel 0.05382.

2. *Graues Zinn*. Aus dem benutzten reinen weissen Zinn bei ÷ 20° hergestellt, ohne Anwendung eines Lösungsmittels:
0.04950; 0.04972; 0.04971; 0.4964; 0.04951, Mittel 0.04962.
Als Differenz ergiebt sich hier $c_w - c_g = 0.00420$.

3. *Weisses Zinn*. Aus dem in Versuch 4 angewandten grauen Zinn bei $^1/_2$ stündigen Erhitzen auf 80° dargestellt:

0.05481; 0.05473; 0.05466, Mittel 0.05473.

4. *Graues Zinn*. Dieses Präparat wurde aus geraspeltem weissem Zinn mittels alkoholischer Pinksalzlösung bei ÷ 20° dargestellt:

0.05056; 0.05056; 0.05065, Mittel 0.05059.

Wir sehen, dass die unter den Abschnitten 3 und 4 angeführten Werte etwas höher sind, als die zuerst angeführten, was leicht zu erklären ist. Bei der Behandlung mit der alkoholischen Salzlösung wird ein Teil des Metalles oxydiert, wodurch eine Erhöhung der spezifischen Wärme stattfindet. Die Differenz der spezifischen Wärmen wird dadurch nur sehr wenig beeinflusst, da die Oxydmenge in den beiden Modifikationen dieselbe ist. Tatsächlich ergiebt sich aus den Abschnitten 3 und 4:

$$c_w - c_g = 0.00414.$$

6. In his second investigation Brönsted has determined the true specific heat of the two modifications at different temperatures between 79.8 and 288°.1 K.

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[1] Zeitschr. für Elektrochemie **20**, 38 (1914).

[2] Zeitschr. für Elektrochemie **18**, 714 (1912); Zeitschr. f. physik. Chemie **88**, 479 (1914).

[3] Zeitschr. f. physik. Chemie **110**, 343 (1924).

[4] Marb. Ber. 1906, S. 196; Ann. der Phys. **22**, 64 (1907).

Table 1 contains the results obtained. From his paper we borrow the following data which are of importance for our further discussion:

„Als Kalorimeter diente bei meinen Versuchen ein Silbergefäss, das etwa 150 g. graues Zinn fassen konnte. Das Kalorimeter wurde zuerst mit grauem Zinn gefüllt und dann mit WOODschem Metall luftdicht zugelötet. Wenn die Versuche mit der grauen Modifikation beendet waren, wurde das Kalorimeter mit Inhalt ungeöffnet eine Stunde auf 60° erhitzt, wobei die Umwandlung in weisses Zinn sich vollzieht. Das in dieser Weise hergestellte weisse Zinn war bei der Temperatur der flüssigen Luft vollkommen beständig, bei — 80° wandelte es sich aber langsam in graues Zinn um, so dass es hier nötig war nicht-umgewandeltes weisses Zinn zu verwenden. Bei Versuchen bei 0° und in flüssiger Luft zeigten sich die beiden Präparate von weissem Zinn identisch".

As BRÖNSTED in his second paper does not give further data about his preparations of tin, we have asked him for information. He writes to us as follows: „In den beiden Arbeiten wurde reines Zinn in Stangen von KAHLBAUM benutzt. Soweit ich sehen kann, wurde in der zweiten Arbeit das graue Zinn frisch hergestellt; die Präparate waren also sicher nicht identisch, wenn auch von gleicher Provenienz".

TABLE 1.
Atomic heat (C_g) of grey tin and (C_w) of white tin (BRÖNSTED).

T	c_w (exp.)	c_g (exp.)
79.8	4.64	3.80
87.3	4.87	4.07
94.8	5.07	4.30
194.9	6.20	5.66
197.2	6.23	5.71
205.2	6.25	5.75
248.4	6.36	5.87
256.4	6.37	5.88
264.3	6.38	5.89
273.0	6.39	5.90
288.1	6.40	5.91

Mean values of about 40 single determinations (mean deviation about 1%).

7. We shall now occupy ourselves with LANGE's investigation, which was published a few months ago. He also determined the specific heats in question, in order to use the values obtained for thermodynamic calculations. His measurements of the true specific heats of the two modif-

ications are carried out in the temperature interval of 9°.60 to 286°.3 K.

As regards the preparations of white and grey tin used he only says in the paper above mentioned: "Das graue Zinn wurde nach den von COHEN gegebenen Vorschriften aus "Zinn KAHLBAUM" hergestellt", and further: "Zu den Messungen (am weissen Zinn) wurden 169.23 g. "Zinn KAHLBAUM" verwandt". We have asked Prof. BODENSTEIN at Berlin for further information, who wrote to us: "Das weisse Zinn ist in Form der von KAHLBAUM gelieferten Stangen benutzt worden; die sind dann geraspelt und nach Ihrer Vorschrift in Pinksalzlösung in graues verwandelt worden unter Verwendung von Keimen von einem Material, das aus dem hiesigen Laboratorium stammte und direkt zur Messung benutzt, unsinnige Werte ergeben hatte. Aus der Pinksalzlösung ist das graue Zinn abfiltriert, mit Alkohol gewaschen und im Vakuum getrocknet worden."

8. Table 2 contains the results of LANGE's measurements. He writes:

TABLE 2.
Atomic heat of grey and white tin (LANGE).

Gray tin 67.49 g.		White tin			
		First series		Second series	
Tm.	*At. H.*	*Tm.*	*At. H.*	*Tm.*	*At. H.*
15.5	0.599	22.4	1.27	9.60	0.206
18.2	0.755	26.9	1.87	10.60	0.266
22.35	1.056	32.7	2.48	11.72	0.346
26.8	1.375	40.9	3.04	12.64	0.435
31.5	1.675	42.5	3.21	13.31	0.477
37.3	2.00	48.0	3.53		
44.9	2.36	56.7	4.06		
52.3	2.80	92.5	5.21		
59.3	3.14	101.1	5.40		
69.5	3.67	286.3	6.27		
92.5	4.42				
102.6	4.73				
283.7	6.13				

Tm is the mean of initial and final temperature during the experiment, in absolute temperatures, while under *At. H.* the atomic heats are given.

"Die gefundenen Werte sind in beiden Fällen [1]) um einen nennenswerten Betrag verschieden gegenüber den BRÖNSTED'schen Messresultaten. Nun aber dürfen die hier mitgeteilten Werte vom weissen Zinn als sehr gesichert gelten, weil beide Messreihen (mit verschiedenen Apparaturen) gut an einander anschliesen und bei höheren Temperaturen eine gute Uebereinstimmung besteht sowohl mit den Messungen von BEHN als auch mit denen von JÄGER und DIESSELHORST. Es ist also anzunehmen, dass die Messungen von BRÖNSTED durch einen systematischen Fehler entstellt sind".

9. LANGE writes about the accuracy of the figures found for the specific heat: "Die Fehlergrenze bei der Bestimmung der auftretenden Temperaturdifferenzen dürfte bei tiefen Temperaturen etwa 1 °/₀, oberhalb von 150 abs. 1.5 °/₀ betragen, so dass entsprechend für die einzelnen spezifischen Wärmen ein Maximalfehler von etwa 1.5 bis 2 °/₀ anzusetzen sein wird".

10. We shall now inquire a little deeper into the investigations mentioned, and consider in how far they offer a guarantee that the preparations of grey and white tin used, indeed satisfy the requirements which ought to be attained in this case.

In BRÖNSTED's as well as in LANGE's researches we look in vain for any criterion, guaranteeing the *physical* purity of the substances. No indication whatever is given enabling us to deduce, that the stabilization into grey tin is in fact complete, neither with the grey tin (see above under 5) which is prepared without the solution of an electrolyte, nor with the preparation which was brought in contact with a solution of pink salt (see above par. 5 under 4). Moreover BRÖNSTED mentions in his second investigation (see above par. 6) a manipulation which leads us to suppose that the material he put into his silver calorimeter, was afterwards, partly at least, transformed into the white modification, even if before this manipulation it had consisted entirely of grey tin. For he solders up the calorimeter with WOOD's metal, an alloy, the melting point of which lies at 71°. Now the velocity of transition of grey tin into white is — as our former investigations [2]) have proved already very considerable [3]) at 35°, and as silver is the metal which, preeminently, conducts heat, the chance is very great that during soldering, the transformation has partly taken place. This is the reason that the values found for the specific heat of grey tin are doubtful.

11. But also as regards the determination of the specific heat of white tin, we remain in doubt, as it was not stated if that white

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[1]) i.e. with the grey as well as with the white tin.

[2]) Zeitschr. f. physik. Chemie **33**, 57 (1900).

[3]) Negative catalysers for this transition are not known up to the present.

tin, prepared from the grey, by heating it to 60° for one hour, had indeed been quantitatively transformed into the white modification. Nevertheless we think it probable that this has indeed been the case.

12. If we now turn to the investigation of LANGE, here also the question arises: what are we to think of the *physical* and *chemical* purity of the substances used?

It is certain that, on account of the method of preparation followed by LANGE, the grey tin was chemically contaminated, in consequence of contact with a solution of pink salt, which causes oxidation. In consequence of the presence of the SnO_2 thus formed, the specific heat of the preparation will increase. But for the rest every criterion is wanting that the white tin has really been transformed into grey. So LANGE's measurements may also relate to mixtures of the two modifications, even putting aside the contamination by SnO_2 which we mentioned above.

13. As LANGE found values for white tin at temperatures, at which BEHN as well as JÄGER and DIESSELHORST also experimented, and his values do not deviate much from theirs, he is of opinion (see above par. 8), not only that these values are correct, but also that BRÖNSTED's measurements are affected with a systematic error. He overlooked the fact that the tin he used which was cast in bars, had not been tested for its *physical* purity, and that the same may be said of the material used by JÄGER and DIESSELHORST. For the investigations of DEGENS [1]), and by WERIGIN, LEWKOJEFF and TAMMANN [2]) as well as those of SMITS and DE LEEUW [3]), and of WERNER [4]), have taught that white tin has a second transition point, and that also at this transition (white, tetragonal tin $\rightleftarrows$ white, rhombic [5]) tin) very persistent retardations take place. As neither JÄGER and DIESSELHORST, nor LANGE paid attention to this fact, we are uncertain about what happened with their tin, when the bars were cast (solidifying of the molten tin). So here too the guarantee for *physical* purity is wanting, and the value of these determinations is wholly fictitious.

14. From what precedes it is evident that we have no guarantee, that either the preparations of BRÖNSTED, grey and white (tetragonal) tin, or LANGE's have been *physically* pure. No significance therefore can be attached to the values of the specific heats of those modifications,

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[1]) Zeitschr. f. anorg. Chemie **63**, 207 (1909).

[2]) Drudes Ann. **10**, 647 (1903).

[3]) These Proceedings **15**, p. 676 (1912).

[4]) Zeitschr. f. anorg. Chemie **83**, 275 (1913).

[5]) In connection with the communications of SPENCER Min. Magaz. **19**, 113 (1921) and of MÜGGE (Centralblatt Min. 1917 pag. 233) we shall not discuss the question whether the form, called rhombic here is rhombic indeed.

which, as it happens, are widely divergent; neither can any value be attached to the thermodynamic calculations, which are based on these figures.

15. As BRÖNSTED, when determining the heat of transition of grey into white (tetragonal) tin, also used a material which had not been checked, the value found for this heat effect also loses its significance.

The investigations treated in this paper, will have to be repeated with a material that is *chemically* as well as *physically* pure. We hope to revert to this subject at a later period.

SUMMARY.

The investigations carried out up to the present time, on the specific heats of grey and white (tetragonal) tin, as well as those made to determine the heat of transition of those modifications, prove again that it is absolutely necessary to be sure of the *chemical*, as well as of the *physical* purity of the substances to be investigated, before they can be used for determining physical constants.

Utrecht, November 1924. VAN 'T HOFF-*Laboratory*.